Journal of the
OPTICAL SOCIETY *of* AMERICA

VOLUME 34, NUMBER 9 SEPTEMBER, 1944

Improved Diffraction Gratings and Replicas

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(Received June 8, 1944)

IN the *Philosophical Magazine* for 1910, I published results of an investigation of the effect of groove form on the distribution of the energy among the various orders of spectra yielded by a diffraction grating. The ruling was done with the natural edge of a selected carborundum crystal, the angle between the edges being 120°. Gratings of one or two thousand lines to the inch, ruled on gold-plated copper plates, were found to have grooves with highly polished sides meeting at an angle of 120°. I emphasized the fact that "*no metal is removed* when the ruling is going on properly, the groove being formed by the compression of the metal." In the following year, in collaboration with Professor Trowbridge of Princeton, similar gratings were ruled with a diamond ground to the proper angle by Professor Brackett.[1]

Gratings of this type, which I called "echelette," proved extremely useful for investigations of the infra-red regions, and a study of the distribution of the intensity with radiations of different wave-lengths, and with different orientations of the groove angle, was carried out in collaboration with Professor Trowbridge and published in subsequent papers.

Replicas made from the rulings, mounted on glass plates and sputtered with gold, were found to perform even better than the originals, in the case of rulings on thin copper plates, which were always far from flat. In a paper entitled "Diffraction gratings with controlled groove form"[2] the ruling of gratings on a film of silver deposited on a polished plate of speculum metal was described. These gratings gave very dark central images, and a very bright first-order spectrum, sometimes giving spectra in which a certain range of color was absent, the dark bands reminding one of the extremely narrow dark bands observed with the curious grating which I described in 1902, which was further studied by Lord Rayleigh, and more thoroughly investigated in 1935.[3] It was not, however, until Strong made his admirable discovery of a method of coating a glass surface with a durable and highly reflecting film of aluminum that we abandoned plates of speculum and made all of our rulings on aluminized plates of Pyrex glass. It was at once apparent that a groove of controlled form and orientation could be ruled on the aluminum, and very high concentration of energy secured in a single spectrum.

Quoting from a letter which I published[4] referring to one of our first aluminum gratings ruled in 1935: "The first large grating ruled on aluminum was a plane one ordered by the Mt.

[1] H. D. Babcock states in his paper in J. Opt. Soc. Am. 34, 1 (1944), that it remained for Anderson in 1916 to begin the practical investigation of the problem, through the introduction of two ideas: (1) the artificial shaping of the diamond, and (2) the formation of the grooves not by cutting or scraping, but by plastic deformation.

[2] Phil. Mag. (Feb. 1912).
[3] R. W. Wood, Phys. Rev. **48**, 928 (1935).
[4] R. W. Wood, Nature **140**, 723 (1937).

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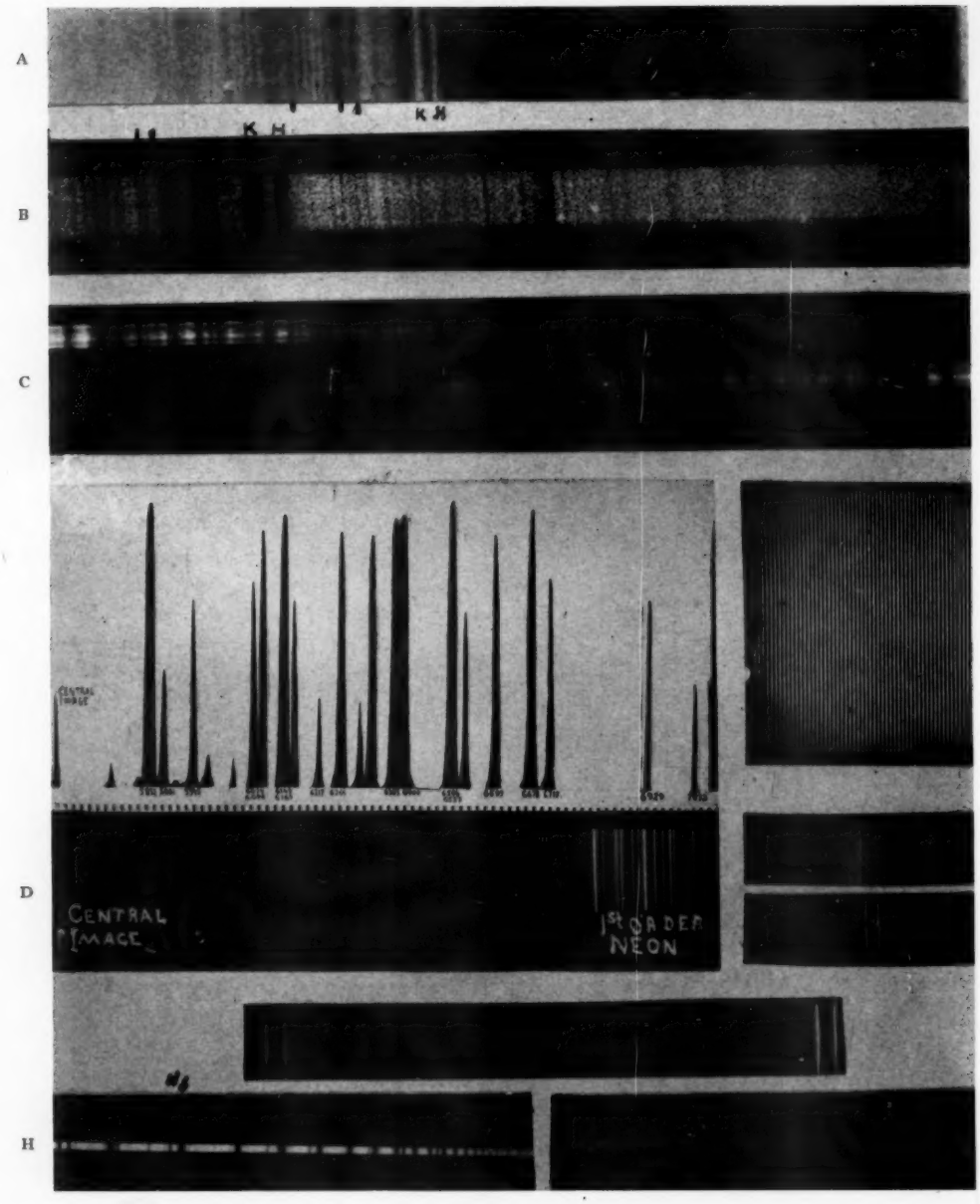


FIG. 1.

Wilson Observatory, 15,000 lines to the inch with a ruled area measuring 4×5.5 inches, and giving 75 percent of the light in the first-order spectrum. This grating has been in constant use in the spectrograph of the 100-inch telescope, and was responsible for the discovery by Dunham of titanium vapor in interstellar space. More recently we have sent a still better grating to this observatory ruled on an 8-inch disk of aluminized Pyrex glass which Dr. Adams reports

as 30 percent brighter than the first. In a letter he tells me that, with the first grating which we sent, he believes that they have made the finest stellar spectrograms ever produced and that in his opinion the day of the glass prism for stellar spectra is over." Two small clippings from a spectrum of α Cygni taken in the second-order spectrum are reproduced in Fig. 1, Part H, one in the vicinity of H_δ, the other extending down to 3100A.

Each grating was tested with a photoelectric cell and galvanometer employing the more intense lines of the quartz mercury arc, for the energy at the central image and lateral spectra, at different angles of incidence. The arrangement of the apparatus is shown in Fig. 2. A vertical quartz mercury arc A is enclosed in a light-tight iron box, close to a wide vertical slit (6×1 cm), the light from which was converged by a lens on the center of the grating G, the central image and various orders of spectra coming to a focus along the dotted line. The grating was mounted on a heavy holder capable of carrying a grating of any size, and provided with a graduated circle by which the alterations of the angle of incidence could be determined. The photoelectric cell was carried on the end of a rod pivoted on the same axis of rotation as that of the grating, and could thus be made to traverse the circle on which the spectral images of the various orders were in focus. Monochromatic radiation was used for each series of readings, obtained by the use of suitable absorbing solutions contained in a glass cell mounted between the arc lens and the slit. A series of observations was made for each of the four monochromatic radiations 4358 and 5461 of mercury, 5893 of a sodium arc in glass, and 7500 from Hg. A typical series for the green mercury line at normal incidence, with galvanometer scale divisions given in cm for the central image and the various orders, is the following:

Order	*Deflection in cm*
2	2.4
1	2.3
0	1.6
1	26.3
2	0.1
3	0.1
	32.8.

To obtain the intensity in the various orders of spectra as percentages of the total diffracted light, we have only to multiply each deflection by 100/32.8 or 3.04, or the percentage in the bright first-order spectrum is $26.3 \times 3.04 = 80$ percent, in the second order $0.1 \times 3.04 = 0.3$ percent, and in the central image $1.6 \times 3.04 = 4.8$ percent.

These values were obtained with a large plane grating ruled with 15,000 lines to the inch ruled for the Department of Physical Chemistry of Harvard University.

The grating was then rotated clockwise and counterclockwise by increments of 5° and readings were taken on all of the spectra for each setting. The complete results for two other gratings are shown in Fig. 3 which shows graphically how the intensity distribution varies with the angle of incidence. Part A was made with a large plane grating giving at normal incidence a high concentration in the region between the blue-green and the red of the first-order spectrum. The directions of the rotations of the grating are indicated by circular arrows at the bottom of the diagram, and the intensity in percentages (shown at left) by the heights of the vertical lines. The "orders" are recorded at the bottom of most of the lines. For the 4358 Hg radiation, the first and second orders have nearly the same intensity (40 and 33) with a clockwise rotation of 10° from normal incidence. Passing back to a counterclockwise rotation of 20° we find that the intensity of the first-order spectrum has risen to 70 percent, while that of the second order has fallen to 4! That such a marked change can be produced by

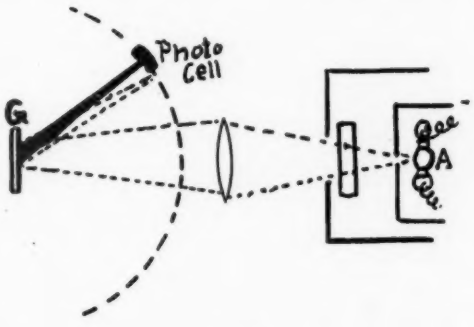
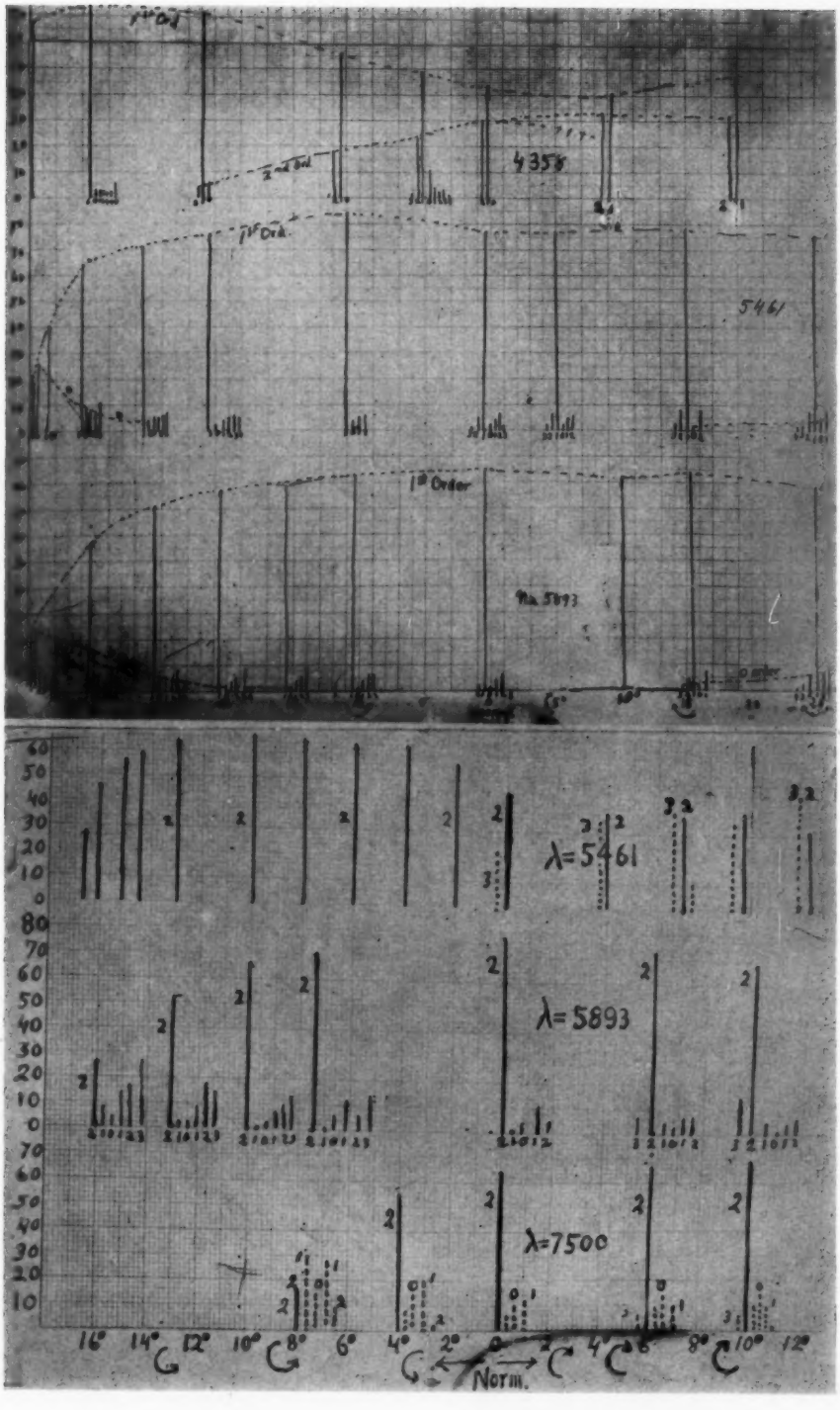


FIG. 2.



A

B

FIG. 3.

altering the angle of incidence is perhaps not realized by the majority of spectroscopists. It is less conspicuous in many gratings, as is shown by Part B of Fig. 3, which was for a grating ruled to give high intensity in the second-order spectrum.

It has been conspicuous in a small apparatus which I have recently constructed for testing the trial rulings (which we always make) for their performance in the ultraviolet down to 2000A, as well as for the finished gratings, which sometimes show that the energy distribution varies in a surprising manner as we pass from one side of the grating to the other. In Fig. 4 rays from a cadmium spark *s* pass through a slit perpendicular to the plane of the paper and, rendered parallel by a quartz fluorite lens *L*, are incident on the grating *G*, the diffracted rays being brought to a focus by the same lens on a semicircular white strip of phosphorescent cardboard *AA*, cut from a sheet of an x-ray intensifying screen. The grating can be rotated, or moved from side to side, to study the relative intensities in the region between 2000 and 4000A depending on the angle of incidence and the portion of the grating utilized. All visible lines appear in their true colors while the ultraviolet lines shine with a yellowish tint.

Replicas made from gratings of proper groove form ruled on a thick aluminum film were found to yield spectra of extreme brilliancy, far brighter than any previously available, the concentration of the light into a single spectrum being comparable to that obtained with the reflecting gratings. The master grating for yielding replicas with most of the energy in the first-order spectrum must be ruled with the diamond set at such an angle that the light is reflected from the wider edge of the groove in the direction of the third-order spectrum for yellow light. The best ones gave so little light in the central image that a strongly illuminated narrow strip of white paper, when viewed through the grating, appeared with a color of, and about as dark as, a piece of chocolate. It was clear that if such replicas could be made of sufficient size they could be used as objective gratings for photographing stellar spectra, and the first experiment in this direction was made in 1939 with a "Schmidt" camera of 3 inches aperture and 5 inches focus, placed at my disposal at the Mt. Wilson Observatory. With a four-inch replica of 7500 lines to the inch placed over the objective of this "pocket" Schmidt, a fully exposed spectrum of Arcturus, 6 mm in length, was obtained with an exposure of 10 seconds, and of the ring nebula in Lyra in 10 minutes. A 30-fold enlargement of the Arcturus spectrum showed lines less than a millimeter in width, and somewhat better resolved than in the same spectrum photographed with the 18-inch Schmidt of 48 inches focus and its monster objective prism at the Mt. Palomar Observatory. The two are reproduced side by side on a slightly different scale in Fig. 1, Part A, a print sent to me by Dr. F. Zwicky at the

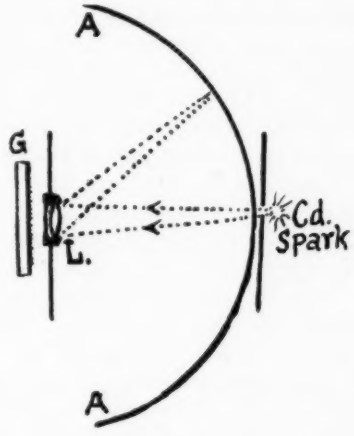


FIG. 4.

time, and Part B, the 30-fold enlargement of the ¼-inch spectrum made with the very small "Schmidt." One is a negative and the other a positive, some identical lines being marked.

Experiments were immediately started on the preparation of a mosaic grating on an 18-inch glass disk for the Mt. Palomar "Schmidt" made by mounting replicas measuring 4×6 inches side by side with their lines accurately parallel. As each element of the mosaic has a much higher resolving power than can be obtained in practice with a slitless spectrograph of this type, it was unnecessary to have the lines "in step." If they are not parallel, however, one obtains spectra in slightly different directions, instead of superposed, and there is consequently a loss of light.

The surprising amount of light thrown into the spectrum of the first order, in the case of one of the 18-inch mosaic gratings for the Mt. Palomar "Schmidt," is shown in Fig. 1, Part D.

The central image and first-order spectrum of a neon tube are reproduced, and above it a greatly reduced photograph of the tracing of a Leeds and Northrup recording densitometer, the regions enclosed by the tracing having been inked in. The central image, which of course contains the light of all of the neon lines, has only the intensity of the faintest lines of the spectrum. Its position is marked by an arrow, and it may well be too faint to show in a reproduction. No trace of any spectra of other orders was recorded. The latest mosaic which I have made has even a higher percentage of light in the first order than this one.

The two disks, 18 inches in diameter and one-half inch thick, of Corning's ophthalmic glass were ground flat and polished by my assistant, Wilbur Perry. One replica was prepared each day, trimmed, and cemented to the disk with the ruled side up. The next replica was placed beside it, with the edges nearly in contact and a portion of both covered with a "test plate," a square of plate glass covered with a similar replica. With the films in contact one sees by transmitted light "shadow bands" which are very narrow and nearly perpendicular to the lines of the grating if the lines are not parallel, but widen and eventually become very broad and parallel to the lines of the gratings when the adjustment for parallelism is perfect. The test plate is turned until the shadow bands formed between it and the cemented replica are broad and parallel to the grating lines, and the second replica is then turned until it is in the proper position. The technique of introducing the cementing fluid is rather involved, and a full description of its details would be too long for the present paper: Moreover, it is being constantly improved, since my first report at the astronomical conference at Tonanzintla in 1942.

To make sure that no cumulative error had occurred, the following test was devised. A telescope was attached with sealing wax to the upper surface of the test plate parallel to the replica lines on the lower surface, and the shadow bands formed in correct position for parallelism on one of the mounted replicas. The disk was now turned into such a position that the point of a distant church spire fell on the cross-hair in the eyepiece. The plate and telescope were then placed over another mounted replica and the shadow bands brought into correct position. If the church spire fell on the cross-hair, the two replicas were proved parallel.

In the preparation of the 24-inch and 36-inch gratings for Harvard's "Oak Ridge" and the Mt. Palomar Schmidt telescopes, the telescope test plate will be employed, since it enables each replica to be brought into parallelism with the central one, thus avoiding the possible cumulative error which might prove troublesome in mounting a larger number of replicas by adjusting each one with respect to the one previously mounted.

Two long narrow strips of plate glass were prepared and covered with replicas adjusted by the telescope. On one the lines are perpendicular to the strip, while on the other they are parallel to it. With these the parallelism of the lines on the mosaic can be adjusted in both azimuths.

To find out the relation between the small angle between the lines of two superposed replicas and the slope of the shadow bands with respect to the direction of the lines on the replica, the following experiment was made: A replica mounted on plate glass was laid in a horizontal position on a ring tripod with the replica side uppermost, and a mirror placed below it which reflected the window light up through the grating. A small telescope, with a vertical spider web in the eyepiece, was cemented with sealing wax to the glass surface of a second mounted replica, the telescope pointing in a direction parallel to the lines. This was laid on the other replica, the grooved surfaces being in contact. Looking down through the gratings, the shadow bands were made wide and parallel to the lines of the gratings. The tripod was then turned until the telescope pointed to a sheet of paper at a distance of 20 feet, and the spider web set on one of two vertical black lines 0.1 inch apart, ruled on the paper. The plate carrying the telescope was then turned until the web coincided with the other black line, and the angle through which the shadow bands turned was found to be 30°, while the telescope had turned through an angle of only two minutes.

The 18-inch mosaic grating was made in 1940 and tried out with the Schmidt at the Mt. Palomar Observatory by Dr. Zwicky in collaboration with the author. Only 800 lines to the inch were employed, as only very short spectra are needed for the classification of stars. Longer spectra would cause overlapping in the case of fields richly populated with stars. With this instrument Zwicky discovered a nova in 1942 while testing the second mosaic which I made. With its bright hydrogen lines it was very conspicuous in the field of stars recorded.

A grating with 1440 lines to the inch has just been completed, since neither the great prism nor the 800-line mosaic will separate the hydrogen line from the nebula line, which will be necessary for distinguishing whether a new object is a nova or an unrecorded planetary nebula.

Another type of grating has been devised for determining the individual velocities of a large number of stars simultaneously, which is now done with an objective prism, and a ray filter of neodymium chloride (the method developed by Pickering and Wood many years ago). An objective prism of small angle is cut in two along a plane parallel to its base and each half covered with a grating replica which deviates the rays in a direction opposite to the deviation given by the prism and of the same amount, the combination being "direct vision." The length of the resultant spectrum is increased by this process, since the deviation of red light is greater than that of violet in the case of the grating, while the opposite is true in the case of the prism. The half-prisms are now mounted, one above the other with the refracting edges to the right and left, respectively, and by properly adjusting the angles, we obtain, when the objective of a telescope or Schmidt camera is covered by the bi-prism grating, two spectra of each star, parallel to each other and lying side by side in the violet region, while the red regions of the two spectra lie to the right and left, respectively. If the star is moving towards the observer the spectra are pushed together in the direction of their length, while if the star is moving away they are drawn apart, the shift of the lines in the violet region with respect to each other being measured in the case of each star. The shift in this case is double that measured with respect to the neodymium absorption line, or with respect to the central image in the case of a grating, since we have two spectra moving in opposite directions.

Preliminary experiments were made with a bi-prism grating of 3 inches aperture in collaboration with Joseph Woods of Baltimore, who had an excellent photographic telescope with a very accurate driving clock. These gave results which looked so promising that I had my assistant, Mr. Perry, prepare a six-inch prism from a thick disk of flint glass. This was cut in two and each half covered with a replica grating giving high intensity in the first-order spectrum mounted on a semicircular glass plate. This was tried out at the Harvard Observatory and gave velocity determinations comparable with those obtained by standard methods. One of the photographs which they obtained is reproduced in Fig. 1, Part C. By adjusting the replica plates with respect to the prisms, and the prisms with respect to each other, it is possible to bring the spectra into contact. In this instance they were separated rather more than is desirable for accurate measurements. The trials were temporarily discontinued owing to the pressure of other work.

ECHELETTE REPLICAS FOR INFRA-RED

Some advance in the preparation of aluminized replicas of echelette gratings has been made recently. Some years ago I prepared a number of such gratings, mounted on selected plate glass (5×7 inches), which were quite favorably reported on by several observers to whom they were sent.

One of the recent ones, ruled for the 3-μ region with 7500 lines to the inch, revealed fine structure in some of the water bands that had never been reported previously, according to a letter received from Professor Harald Nielsen, who also reported far better resolution of the lines of the HCl band than was obtained by Levin and Meyer.

Four master rulings have been made on copper plates, such as are furnished for halftone reproductions, with spacings of 1000, 1800, 3600, and 7500 lines to the inch. These plates, prepared by the Edes Company of Plymouth by a new

polishing technique, are practically free from the "orange peel" structure of those formerly employed. As I have carefully explained to investigators hopefully requesting "original rulings" and *not* replicas, the replicas as now made are vastly superior to the originals, as is clearly shown by Part F of Fig. 1, in which the upper spectrum of the *D* lines of sodium was made with a telescope of 8 inches aperture and 8-foot focus in the thirteenth order of the master grating (1800 lines to the inch), while below it we have the *D* lines as recorded by the replica. The explanation, as mentioned previously, is that, while the copper plates have a beautiful surface, they are far from flat, having slight undulations in various azimuths. These are all "ironed out" when the replica is pressed down into contact with the surface of the plate glass.

Part G, Fig. 1 shows the *D* lines in the 30th and 32nd orders (into which practically all of the energy is concentrated) of a grating having 1000 lines to the inch. In this grating the sides of the grooves which reflect the light in the direction of these two spectra are so perfect that even with a path difference of 31 wave-lengths between the wavelets reflected from adjacent steps of this grating, which is in fact a reflecting *echelon*, we have surprisingly good resolving power.

A microphotograph of the surface of the master grating, made under conditions of illumination such that the light reflected in the direction of these two high orders entered the microscope, is reproduced in Part E, Fig. 1 which has the appearance of a wire grating by transmitted light, with equal widths of dark and light areas. Spectra of even orders are absent with such a grating, and I am awaiting with interest a report on the performance of replicas from this grating in the 20-μ region, in regard to "absent" spectra.

We abandoned years ago the manufacture of echelette gratings ruled on thick copper disks with so-called optically flat surfaces, owing to the impossibility of obtaining plates free from embedded abrasive, which destroyed the sharp edge of the ruling diamond.

The aluminized replicas which I made several years ago differ from these newer ones in that the concentration was spread over a larger number of spectra when examined by sodium light. A former one of 1000 lines, instead of concentrating practically all of the light in the 30th and 31st orders, distributed it rather uniformly over eight or ten orders, and I am interested to know whether this high concentration in one or two orders with visible light is advantageous when the grating is used in the infra-red. That replicas of such good and uniform performance can be made in quantity should be of interest to those desiring high resolution in the infra-red region of the spectrum.

Expenses incurred in connection with the preparation of the first 18-inch mosaic grating were met by a grant from the Rumford fund of the American Academy of Arts and Sciences.

JOURNAL OF THE OPTICAL SOCIETY OF AMERICA VOLUME 34, NUMBER 9 SEPTEMBER, 1944

Criteria for Resolution and the Resolving Power of Absorbing Prisms

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(Received March 27, 1944)

A method is outlined by which the limiting resolving power of any prism may be readily determined. It has been necessary to redefine the limit of resolution as the minimum angular separation of the central maxima of the individual diffraction images at which there may exist a minimum of total intensity between the positions of the individual central maxima. Application to a 10-cm rocksalt prism is included.

I. CRITERIA FOR RESOLUTION

RECENT improvements in thermocouple and amplifier designs have made it possible to construct an infra-red prism spectrometer having a resolving power approximately equal to that of the prism itself. Moreover, in order to take advantage of the increased dispersion of the prism material as the wave-length approaches the fundamental absorption region, it is customary to extend the measurements with a given prism to wave-lengths for which the absorption by the prism is very strong. The determination of the ideal resolving power of absorbing prisms thus becomes a problem of some practical importance.[1]

Lord Rayleigh's criterion for resolution, as usually stated, defines resolution in terms of the angular separation of the rays corresponding to the positions of the central maximum and the first minimum of the diffraction image.[2] While this arbitrary definition has proven satisfactory for the comparison of systems having uniform illumination across their apertures, it does not correctly define a physical limit of resolution; and when applied to the case of absorbing prisms, it leads to results which are obviously unreasonable. For example, the limiting resolving power of a non-absorbing prism is underestimated by nearly 17 percent, and the Rayleigh resolving power of absorbing prisms decreases discontinuously with decreasing transmission. Hence, for the purpose of the following discussion, the criterion for resolution has been redefined as follows: *The limit of resolution is the minimum angular separation of the central maxima of the individual diffraction images at which there may exist a minimum of total intensity between the positions of the individual central maxima.*

In the evaluation of the resolving power $\lambda/\Delta\lambda$, it is convenient to define $\Delta\lambda$ as the wave-length separation, at the wave-length λ, corresponding to the limit of resolution of two equivalent, symmetrical lines. Since now the total intensity pattern is symmetrical about a point midway between the individual central maxima, it is a simple matter to determine the conditions necessary for the existence of a central minimum of total intensity.

Let $I(\theta)$ be the intensity of one of the lines as a function of θ, the angular distance from its central maximum. With a line separation of $2\theta_0$, the total intensity at the center is $2I(\theta_0)$, and the total intensity at a displacement of $d\theta$ from the center is $I(\theta_0+d\theta)+I(\theta_0-d\theta)$. For the total intensity at the center to be a minimum, it is required that

$$I(\theta_0+d\theta)+I(\theta_0-d\theta)\geq 2I(\theta_0). \qquad (1)$$

Upon expansion about θ_0, with neglect of terms in $(d\theta)^3$ and higher, this becomes

$$(d^2I/d\theta^2)_{\theta_0}\geq 0. \qquad (2)$$

Thus the limit of resolution of two equivalent, symmetrical lines may be defined as twice the angular separation of the central maximum from the first point of inflection of one of the lines.

[1] The resolving power of spectrometers under conditions such that the limiting factor is the finite slit widths necessary to obtain the minimum energy required for measurement has been discussed by J. Strong, Phys. Rev. **37**, 1661 (1931).

[2] Rayleigh's statement in the *Encyclopaedia Britannica*, Vol. XXIV (1888), is: "We conclude that a double line cannot be fairly resolved unless its components subtend an angle exceeding that subtended by the wave-length of light at a distance equal to the horizontal aperture." Note that this statement contains no basis for distinguishing between the cases of the absorbing and the non-absorbing prisms.

II. CALCULATION OF THE LIMIT OF RESOLUTION

Reese[3] has derived expressions for I, $dI/d\theta$, and $d^2I/d\theta^2$ for the diffraction images of absorbing prisms. Since in all practical applications the interesting values of θ are of the order of magnitude of λ/W, where W is the horizontal aperture of the beam exit from the prism, it is convenient to simplify his results by using the approximation $\theta \simeq \sin\theta$. Setting $w=2\pi W/\lambda$, $Z=(f^2+\theta^2)$, and $E=1+e^{-2fw}-2e^{-fw}\cos w\theta$, one obtains

$$I=KE/Z, \tag{3}$$

$$dI/d\theta=K(2we^{-fw}Z\sin w\theta-2\theta E)/Z^2, \tag{4}$$

$$d^2I/d\theta^2=K[2w^2e^{-fw}Z^2\cos w\theta+8\theta^2E -2Z(4w\theta e^{-fw}\sin w\theta+E)]/Z^3. \tag{5}$$

Here K is a constant related to the intensity of the light beam incident upon the prism and f is a constant related to the absorption coefficient k of the prism material; $2fw=kM$, where M is the maximum path length through the prism.

The limit of resolution $2\theta_0$ is obtained from the smallest value $\theta=\theta_0$ which, for a given f and w, satisfies the equation $d^2I/d\theta^2=0$. To facilitate the solution for θ_0 by numerical approximation, the substitution $\theta=rf$ is made in (5) and the expression multiplied by $f^4(1+r^2)^3e^{fw}/2K$ to give[4]

$$\{(2+f^2w^2)+r^2[r^2f^2w^2+(2f^2w^2-6)]\}\cos rfw -4rfw(1+r^2)\sin rfw+(6r^2-2)\cosh fw=0. \tag{6}$$

Notice that here r, and hence rfw, is a function of the product fw. Furthermore,[5]

$$\lim_{fw\to 0} rfw=2.606\cdots, \tag{7}$$

$$\lim_{fw\to\infty} rfw=3^{-\frac{1}{2}}fw. \tag{8}$$

TABLE I.

fw	rfw
0.0	2.606
0.5	2.613
1.0	2.631
2.0	2.708
3.0	2.843
4.0	3.041
5.0	3.314
6.0	3.666
7.0	4.101
8.0	4.609
10.0	5.751

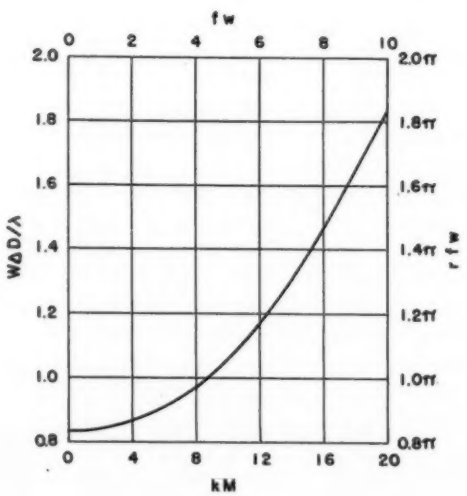

FIG. 1.

Values of rfw which satisfy (6) for intermediate values of fw are given in Table I, and rfw is plotted as a function of fw in Fig. 1 (reading top and right coordinates). Since $2fw=kM$ and $2\theta_0=2rfw/w=2rfw\lambda/2\pi W=\Delta D$, the difference between the deviations by the prism of the two equivalent lines at the limit of resolution, Fig. 1 also shows $W\Delta D/\lambda$ as a function of kM (reading bottom and left coordinates). In the limit $kM\to\infty$, or, for practical applications, for $kM>16$,

$$\Delta D=\lambda kM/2\cdot 3^{\frac{1}{2}}\pi W=\lambda kM/10.883W. \tag{9}$$

III. PRISM RESOLVING POWER

The general treatment of prism resolving power is complicated by the necessity of determining whether the horizontal aperture of the exit beam is limited by the length of the front

[3] H. M. Reese, Astrophys. J. 13, 199 (1901).

[4] This is valid for all values of f since, as $f\to 0$, $r\to\infty$ in such a way that rf is finite.

[5] The limiting values given in (7) and (8) are obtained from the equations

$$6+(r^3f^2w^3-6)\cos rfw-4rfw\sin rfw=0 \tag{6a}$$

and

$$6r^2-2=0 \tag{6b}$$

to which (6) may be reduced in the limits $fw\to 0$ and $fw\to\infty$, respectively. Note that w is finite and $\gg 0$ since $W\gg\lambda$.

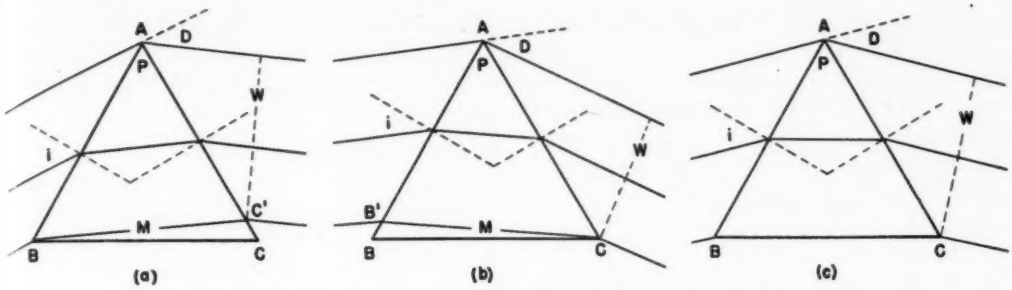

FIG. 2. Geometrical relations for various optical paths through the prism.

Given:

P, the prism angle.
$F=\overline{AB}$, the length of the front face of the prism.
$R=\overline{AC}$, the length of the rear face of the prism.
$L=\overline{BC}$, the length of the base of the prism.
i, the angle between the incident light beam and the normal to the front face of the prism.
n, the index of refraction of the prism material at the wave-length λ.
$N=(n^2-\sin^2 i)^{\frac{1}{2}}$.
$G=N\sin P-\sin i\cos P$.
$H=N\cos P+\sin i\sin P$.

Derived:

D, the deviation of the light beam by the prism.
M, the maximum path length through the prism of any ray in the exit beam.
W, the width of the exit beam.

(a) Case I, F limits horizontal aperture.
$D=i-P+\sin^{-1}G$.
$dD/dn=(n\sin P)/[N(1-G^2)^{\frac{1}{2}}]$.
$M=(nF\sin P)/H$. $W=FN(1-G^2)^{\frac{1}{2}}/H$.

(b) Case II, R limits horizontal aperture.
$D=i-P+\sin^{-1}G$.
$dD/dn=(n\sin P)/[N(1-G^2)^{\frac{1}{2}}]$.
$M=(nR\sin P)/N$. $W=R(1-G^2)^{\frac{1}{2}}$.

(c) Minimum deviation, equal lengths S, illuminated on front and rear faces of prism. Let S be the face length of a completely illuminated isosceles prism of angle P and base length L.
$D=2\{\sin^{-1}[n\sin(P/2)]-(P/2)\}$.
$dD/dn=[2\sin(P/2)]/[1-n^2\sin^2(P/2)]^{\frac{1}{2}}$.
$M=L=2S\sin(P/2)$. $i=\sin^{-1}[n\sin(P/2)]$.
$W=L[1-n^2\sin^2(P/2)]^{\frac{1}{2}}/[2\sin(P/2)]$
$=S\cos i=L/(dD/dn)$.

face of the prism, Case I, or by the length of the rear face of the prism, Case II. Figure 2 illustrates these cases and gives the values of the derived geometrical relations which are required for the determination of the resolving power. The special case of minimum deviation is also included because of the extensive use of minimum deviation mountings in prism spectrograph construction.

Given P, F, R, i, λ, n, $dn/d\lambda$, and k, the steps in the procedure for determining the resolving power may be as follows:[6]

(1) Determine W for Cases I and II. Use the smaller value in further computations.

(2) Determine M for the case which yields the smaller W.

(3) From kM, obtain $W\Delta D/\lambda$ from Fig. 1 or Table I and calculate ΔD [or, if $kM>16$, calculate ΔD from (9)].

(4) Calculate $\Delta\lambda=\Delta D/(dD/dn)(dn/d\lambda)$ and the resolving power $=\lambda/\Delta\lambda=\nu/\Delta\nu$.

[6] It is assumed throughout that n, $dn/d\lambda$, and k are evaluated at the given wave-length λ.

In the ranges $0<kM<1$ and $kM>16$, explicit expressions for the limiting resolving power, L.R.P., which are accurate to within one percent may be written as

$$0<kM<1: \quad \text{L.R.P.}=1.2W(dD/dn)(dn/d\lambda)$$
$$=1.2\ \text{R.R.P.}(0), \quad (10)$$

and

$kM>16$:

$$\text{L.R.P.}=10.88W(dD/dn)(dn/d\lambda)/kM, \quad (11)$$

where R.R.P.(0) represents the Rayleigh resolving power for $k=kM=0$.

In the special case of a completely illuminated isosceles prism, of base length L, at minimum deviation, (10) and (11) become

$$0<kL<1: \quad \text{L.R.P.}=1.2L(dn/d\lambda) \quad (12)$$

and

$$kL>16: \quad \text{L.R.P.}=10.88(dn/d\lambda)/k. \quad (13)$$

IV. INADEQUACY OF THE RAYLEIGH CRITERION

Rayleigh's own statement of the criterion for resolution[2] is obviously arbitrary and not intended to apply under conditions of non-uniform

intensity across the aperture. The usual statement of Rayleigh's criterion, that for two lines to be resolved the "distances between the central maxima of their diffraction images must be at least as great as the distance of the first minima from the central maximum,"[7] leads to values of ΔD which increase exponentially with kM as $kM \to \infty$. These values of ΔD are absurdly large for values of kM for which the prism transmission $T=(1-e^{-kM})/kM$ (or $T \simeq 1/kM$ for large kM) is still sufficiently large to be of experimental value. This is illustrated by Fig. 3 in which $W\Delta D/\lambda = W\theta_0'/\lambda$ is plotted against T. (Figure 3 also shows $W\Delta D/\lambda$ as the function of T determined by our redefined limit of resolution.) The angle between the central maximum and the first minimum, $\theta_0'=sf$, is determined from the smallest non-zero value of sfw which satisfies the equation

$$2\cos sfw+\left(s+\frac{1}{s}\right) fw \sin sfw - 2\cosh fw=0. \quad (14)$$

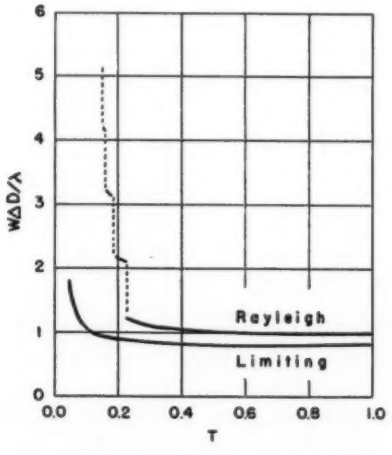

FIG. 3.

This equation representing the condition for the existence of a minimum or maximum in $I(\theta)$ is obtained from (4) by substituting $\theta=sf$, multiplying by $f^3(1+s^2)^2e^{fw}/2Ks$ and equating to zero.[8]

The lower limiting value of sfw corresponding to the first minimum is

$$\lim_{fw\to 0} sfw=2\pi.$$

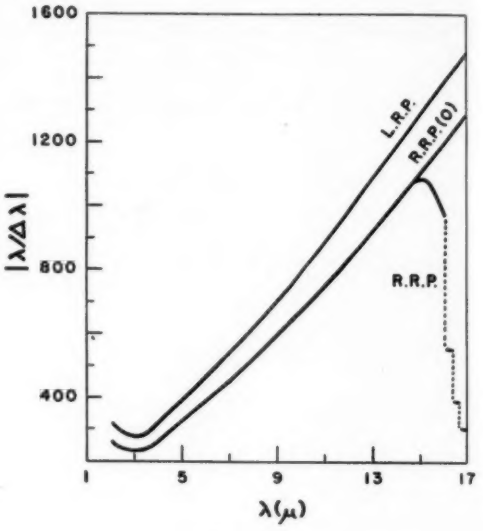

FIG. 4.

As $fw \to \infty$, sfw approximates in a discontinuous manner, at intervals of 2π, the function e^{fw}.

V. APPLICATION TO ROCKSALT PRISM

As an application, consider the special case of a completely illuminated 10-cm equilateral prism of rocksalt at minimum deviation. Figure 4[9] shows both the limiting resolving power (L.R.P.) and the Rayleigh resolving power (R.R.P.) for such a prism as a function of the wave-length $\lambda(\mu)$ at 25°. In addition is plotted the Rayleigh resolving power of a non-absorbing prism, R.R.P.(0), of the same dimensions and dispersion.

[7] See, for example, R. W. Wood, *Physical Optics* (The Macmillan Company, New York, 1934), third edition, p. 251.

[8] H. M. Reese (reference 3) discusses in some detail the determination of minima and maxima in $I(\theta)$.

[9] In the calculation of $\lambda/\Delta\lambda$ for rocksalt, n and $dn/d\lambda$ were obtained from the data of F. Paschen [Ann. d. Physik **26**, 120 (1908)] as corrected to 25° by P. C. Cross [Rev. Sci. Inst. **4**, 197 (1933)]. The values of k were determined from the transmission data of H. Rubens and A. Trowbridge [Ann. d. Physik **60**, 724 (1897)].

The Energies of Polyatomic Molecules*

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THE vibration-rotation term values of a polyatomic molecule may, except in anomalous cases, be obtained to a good approximation by solving for the roots of the secular determinant of the matrix H, which has the following elements:

$$(v, J, K|H|v, J, K) = (E_v/hc)+\tfrac{1}{2}(X_v+Y_v)[J(J+1)-K^2] + Z_v K^2+2Z_e \textstyle\sum_r \zeta_r l_r K - D_J J^2(J+1)^2 - D_{JK}J(J+1)K^2 - D_K K^4, \quad (1a)$$

$$(v, J, K|H|v, J, K\pm 2) = \tfrac{1}{2}(X_v - Y_v)\{[J(J+1)-K(K\pm 1)] \times [J(J+1)-(K+1)(K+2)]\}^{\frac{1}{2}}, \quad (1b)$$

where (E_v/hc) is the vibrational energy and is equal to

$$(E_v/hc) = \textstyle\sum_s \omega_s(v_s+g_s/2) + \sum_s \sum_{s'} x_{ss'}(v_s+g_s/2)(v_{s'}+g_{s'}/2) + \sum_r \sum_{r'} x_{l_r l_{r'}} l_r l_{r'}. \quad (2)$$

In the above, X_v, Y_v, and Z_v are the effective reciprocals of inertia $X_v = X_e - \sum_s x_s(v_s+g_s/2)$, $Y_v = Y_e - \sum_s y_s(v_s+g_s/2)$, etc., the quantities X_e, Y_e, and Z_e being, respectively, equal to $(h/8\pi^2 I_{xx}^{(e)} c)$, $(h/8\pi^2 I_{zz}^{(e)} c)$, etc. v_s is the total vibration quantum number characteristic of an energy level associated with the normal frequency ω_s, J is the quantum number of total angular momentum, and K is the quantum number of angular momentum directed along a preferred axis in the molecule (i.e., $K \leqslant J$). If the frequency ω_r is twofold degenerate there exists another quantum number l_r, which takes the values $\pm(v_r)$, $\pm(v_r-2)$, $\cdots$ and determines the amount of internal angular momentum which is associated with the vibration energy levels of the frequency ω_r. If several twofold oscillations are excited at once, the total internal angular momentum of vibration will be characterized by $\sum_r l_r$. When the frequencies ω_s are threefold degenerate, the vibration energies become too complicated for this discussion. It is preferable to treat molecules where such vibrations occur as anomalous. The fourth term in (1a) is a first-order Coriolis interaction term which arises out of a coupling of the angular momentum K to the angular momentum $\sum_r l_r$ associated with the twofold degenerate oscillations. (It is here assumed that the twofold degenerate oscillations ω_r are perpendicular to the axis z.) g_s is used to denote the order of the degeneracy of the oscillation. ζ_r may be called the coupling coefficient and depends in an involved manner upon the nature of the normal coordinates associated with ω_r. It is worthy of note that the elements of H/hc are diagonal in all the quantum numbers, vibrational and rotational, except the quantum number K.

In the above relations $x_{ss'}$ and $x_{l_r l_{r'}}$ are the anharmonic corrections to the vibration energies which depend in a complicated manner on the coefficient multiplying the anharmonic terms in the potential energy. The constants x_s, y_s, and z_s are corrections to the reciprocals of inertia of the molecule arising from the fact that the molecule as a rotator is only semirigid. These depend upon the size and shape of the molecule and upon the anharmonic portion of the potential energy. D_J, D_{JK}, and D_K are the centrifugal distortion coefficients which depend essentially on the size and shape of the molecule and upon the nature of the normal vibrations. The quantities $x_{ss'}$, $x_{l_r l_r}$, x_s, etc., might all be expected to be small magnitudes. For all symmetric molecules $X_v = Y_v$ so that the $(K|H|K \pm 2)$ elements vanish and hence the energies are equal just to the elements (1a).

Not infrequently, however, it is found experimentally that the $x_{ss'}$ and the x_s, y_s, and z_s are not as small as might have been anticipated. In some cases the relation (2) is actually found to be incompatible with the experimental results altogether. Theoretical researches have shown that such a divergence between experiment and

* Paper presented by invitation at the Winter Meeting of the Optical Society of America, held in New York City, March 2–4, 1944.

the results of relation (2) might be expected if certain of the vibration frequencies of the molecule become accidentally degenerate. For example, if the anharmonic potential energy contains a term $k_{sss'}q_s^2q_{s'}$ connecting the frequencies ω_s and $\omega_{s'}$ then there will occur in the second-order corrections terms $x_{ss'}$ of the vibration energies a term containing the denominator $(2\omega_s-\omega_{s'})$. If accidentally $2\omega_s\approx\omega_{s'}$ resonance is said to take place and this term may become indefinitely large. It has been demonstrated by Fermi[1] and subsequently enlarged upon by Dennison[2] that in such cases it is necessary to treat the overtone frequency $2\omega_s$ and the fundamental $\omega_{s'}$ as degenerate frequencies. This causes certain of the matrix components of the term $k_{sss'}q_s^2q_{s'}$ which are non-diagonal in the vibration quantum numbers, $(v_sv_{s'}|v_s\pm2,\ v_{s'}\mp1)$, to become of first-order significance. If the oscillation ω_s is non-degenerate one quickly obtains for the $(v_s, v_{s'}|k_{sss'}q_s^2q_{s'}|v_s\pm2, v_{s'}\mp1)$ elements of $k_{sss'}q_s^2q_{s'}$:

$$(v_s,\ v_{s'}|H/hc|v_s+2,\ v_{s'}-1)$$
$$=(k_{sss'}/2)\{(v_s+1)(v_s+2)(v_{s'}/2)\}^{\frac{1}{2}}, \quad (3)$$

and if the oscillation ω_r is twofold degenerate it may be shown that the corresponding elements are:

$$(v_r,\ l_r,\ v_{s'}|H/hc|v_r+2,\ l_r,\ v_{s'}-1)$$
$$=(-k_{rrs'}/2)\{[(v_r+2)-l_r^2][v_{s'}/2]\}^{\frac{1}{2}}. \quad (4)$$

To obtain the energies one proceeds to solve for the roots of the secular determinant which has the elements (1a), (1b) and now also the elements (3) or (4) as well. The diagonal elements (1a) will now be altered, but only to the extent that the terms in $x_{ss'}$ and $x_{l_rl_{r'}}$ will no longer contain terms with the resonance denominators $(2\omega_s-\omega_{s'})$. The elements (1) and (3) or (4) are diagonal in all the vibration quantum members except v_s and $v_{s'}$. If we group the elements involving v_s and $v_{s'}$ together we shall have a determinant composed of elements along the principal diagonal and boxes centered about the diagonal which contain the elements (3) or (4) belonging to the states which have nearly equal energies. We shall illustrate this by reference to the pair of states $v_s=2$, $v_{s'}=0$, and $v_s=0$ and $v_{s'}=1(J=K=0)$ which evidently would be degenerate if $2\omega_s\approx\omega_{s'}$. The elements (3) are equal to $(k_{sss'}/2)$. The secular determinant will therefore have the form:

$$\begin{vmatrix} x & & & & & & \\ & x & & & & & \\ & & x & & & & \\ & & & (2,0) & (0,1) & & \\ & & & (2,0) & E_{2,0}-W & (k_{sss'}/2) & \\ & & & (0,1) & (k_{sss'}/2) & E_{0,1}-W & \\ & & & & & x & \\ & & & & & & x \end{vmatrix} =0. \quad (5)$$

The roots will be equal to the diagonal elements outside of the box and the two other roots.

$$W=\tfrac{1}{2}[E_{2,0}+E_{0,1}]\pm\tfrac{1}{2}\{[E_{2,0}-E_{0,1}]^2 + k_{sss'}{}^2\}^{\frac{1}{2}}. \quad (6)$$

The effect of the perturbation on the two levels is to cause them to be separated from each other by an anomalously large amount so that the bands which would occur when the molecule makes a transition from the normal state to the states $E_{2,0}$ and $E_{0,1}$ will be displaced from their unperturbed positions. It is, in reality, no longer legitimate to speak of the two frequencies as $2\omega_s$ and $\omega_{s'}$ since each of the resonating levels now has some of the characteristics of both of the levels $2\omega_s$ and $\omega_{s'}$. It is customary to denote them rather by $(2\omega_{s'}:\omega_{s'})$ and $(\omega_s:2\omega_{s'})$, respectively. The one will occur at too high a frequency and the other at too low a frequency. The perturbation affects principally the positions of the band centers, but at the same time there is also a "mixing" of the effective moments of inertia of the molecule in these states so that the rotational structure of the bands will also be altered slightly. Another effect of the perturbation is that the intensity with which the transition occurs will be altered. For example, the band $(2\omega_{s'}:\omega_{s'})$ is an overtone and might be expected to occur with only a small intensity. Because of the degeneracy there is a "mixing" of the wave functions associated with these states and it becomes possible for the harmonic band to borrow intensity from the fundamental to the extent that it becomes quite a prominent band

[1] E. Fermi, Zeits. f. Physik **7**, 250 (1931).
[2] D. M. Dennison, Phys. Rev. **41**, 304 (1932).

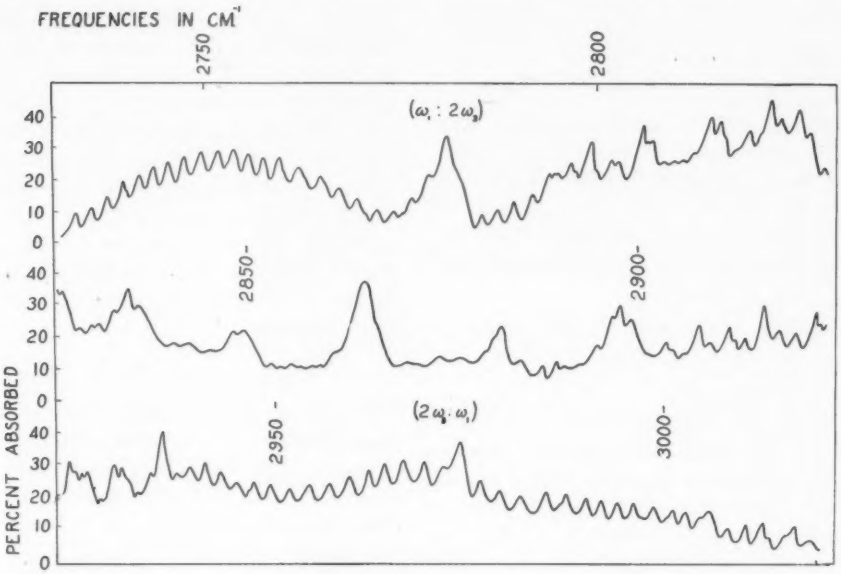

FIG. 1. Infra-red absorption spectrum of formaldehyde vapor near 3.3μ showing the resonating parallel vibrations (ω_1:$2\omega_2$) and ($2\omega_3$:ω_1).

in the spectrum. This is notably true in the case of CO_2 where $2\omega_2$ is nearly coincident with ω_1, but it has also been observed in the case of several hydrocarbons. In the case of the spectrum of formaldehyde vapor (Fig. 1) it seems probable that the two parallel type bands of 2780 cm^{-1} and 2974 cm^{-1} are jointly due to transitions from the normal state to the resonating pair of levels ω_1 and $2\omega_3$. Both parallel type bands are quite intense.

Another type of term which may occur in the anharmonic portion of the potential energy and may produce resonance is the term $k_{ss's''}q_sq_{s'}q_{s''}$. This problem has not been studied, but it might be dealt with as suggested in the foregoing. It gives rise in the constant $x_{ss'}$ to terms with the denominators $(\omega_s+\omega_{s'}-\omega_{s''})$ and $(\omega_s-\omega_{s'}-\omega_{s''})$. If any of these denominators should become very small resonance will again occur. It is worthy of observation that when resonance occurs in first order of approximation between two vibration frequencies it is always between a fundamental and a combination frequency or overtone; never between two fundamentals or two harmonics.

A second kind of resonance which is similar to the one discussed in the foregoing was discovered by Darling and Dennison[3] in their analysis of the water vapor spectrum. This interaction makes itself felt in second-order approximation. For example, the quartic part of the potential energy function will contain a term $k_{ss's'}q_s^2q_{s'}^2$. Normally one is interested only in the diagonal elements $(v_s, v_{s'}|v_s, v_{s'})$ of this term when evaluating the constants $x_{ss'}$ to second order of approximation. If the calculation were carried to still higher approximations, terms would be present in $x_{ss'}$ which would contain the denominator $(2\omega_s-2\omega_{s'})$. If, however, $2\omega_s\approx 2\omega_{s'}$ this term may become extremely large. As before one must treat $2\omega_s$ and $2\omega_{s'}$ as degenerate, the non-diagonal elements $(v_s, v_{s'}|v_s\pm 2, v_{s'}\mp 2)$ now becoming of second-order significance. Terms of the type $k_{sss'}q_s^2q_{s'}$ may also contribute to the above type of resonance. Normally if we concern ourselves with the energies to second order of accuracy we should be interested only in the matrix elements

$$(v_sv_{s'}|k_{sss'}q_s^2q_{s'}|v_s'v_{s'}')(v_s'v_{s'}'|k_{sss'}q_s^2q_{s'}|v_sv_{s'}).$$

There are, of course, others. For example, the

[3] B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).

elements

$$(v_s v_{s'} | k_{sss'} q_s^2 q_{s'} | v_s+2, (v_{s'}-1) \times (v_s+2, v_{s'}-1 | k_{sss'} q_s^2 q_{s'} | v_s+2, v_{s'}-2)$$

which would normally contribute to the energy only in an approximation beyond the second become of the second-order significance and must be taken into account if $2\omega_s \approx 2\omega_{s'}$. Specifically applied to water vapor type molecules where resonances occur between $2\omega_1$ and $2\omega_3$ we have

$$\begin{aligned}(v_1, v_2, v_3 | v_1-2, v_2, v_3+2) &= (\tfrac{1}{2})[v_1(v_1-1)(v_3+1)(v_3+2)^{\frac{1}{2}}] \\ &\times [(k_{1133}/4) - (2\pi c k_{133}^2/\omega_3) \\ &+ (\pi c k_{111} k_{133}/\omega_1) \\ &+ (\pi c k_{233} k_{111}/\omega_2)(\omega_2^2/(4\omega_3^2-\omega_2^2))).\end{aligned}$$

The energies are obtained as in the previous example by solving for the roots of the secular determinant which has the diagonal elements (1a) (which this time are unaltered) and now also the non-diagonal elements of second-order magnitude. The non-diagonal elements belonging to the frequencies which are nearly alike are grouped together in boxes on either side of the diagonal. Diagonalization is entirely analogous to the preceding example where each little box is diagonalized separately. In Table I we give the observed positions of certain vibration levels in the water vapor spectrum, the predicated positions of these levels if the resonance is neglected, and the predicted positions if the resonance is taken into account. In this case the resonance is between the overtones $2\omega_s$ and $2\omega_{s'}$ and not the fundamentals ω_s and $\omega_{s'}$. In the spectrum the positions of the fundamental bands remain unaffected.

In general other second-order resonance interactions between vibration frequencies may take place. For example, if a term $k_{ss's''} q_s q_{s'} q_{s''}^2$ can occur in the potential energy function a second-order resonance interaction may exist between the two fundamentals ω_s and $\omega_{s'}$. If a term $k_{ssss'} q_s^3 q_{s'}$ may be present resonance between the fundamentals ω_s and the overtone $3\omega_{s'}$ may exist. Resonance may also occur between other combinations of frequencies, but the above are probably the most important. A more complete discussion is beyond the scope of this paper.

There remains still another type of interaction which contributes to the corrections x_s, y_s, and z_s to the effective reciprocals of inertia.[4] These are the Coriolis type of interactions which arise from the presence in kinetic energy of terms which have the form:

$$\zeta_{ss'}[(\omega_{s'}/\omega_s)^{\frac{1}{2}} q_s p_{s'} - (\omega_s/\omega_{s'})^{\frac{1}{2}} q_{s'} p_s] P_\alpha, \qquad (6)$$

where P_α are the operators corresponding to the components of the angular momentum directed along the axes x, y, and z fixed in the molecule and $\zeta_{ss'}$ is the Coriolis coupling coefficient which depends in a complicated manner on the normal coordinates associated with ω_s and $\omega_{s'}$. These terms have no elements diagonal in the vibration quantum numbers and hence do not, under normal conditions, contribute to the energy before in second order of approximation. They contribute a term which tends to increase the effective reciprocal of inertia for the higher of the two frequencies ω_s and $\omega_{s'}$ and tends to decrease the reciprocal of inertia associated with the lower of the two frequencies. This term

TABLE I.

$v_1 v_2 v_3$	$(W/hc)_{obs.}$	(W/hc) Calculated neglecting resonance	(W/hc) Calculated observing resonance
(2, 0, 1)	10613.1 cm^{-1}	10662.8 cm^{-1}	10617.1 cm^{-1}
(0, 0, 3)	11032.4	10982.4	11028.0
(2, 1, 1)	12151.2	12195.1	12150.3
(0, 1, 3)	12565.0	12521.7	12566.5
(3, 0, 1)	13830.9	13984.4	13834.4
(1, 0, 3)	14318.8	14167.4	14317.2
(3, 1, 1)	15347.9	15494.5	15346.8
(1, 1, 3)	15832.5	15684.5	15832.2

[4] H. H. Nielsen, J. Chem. Phys. 5, 818 (1937).

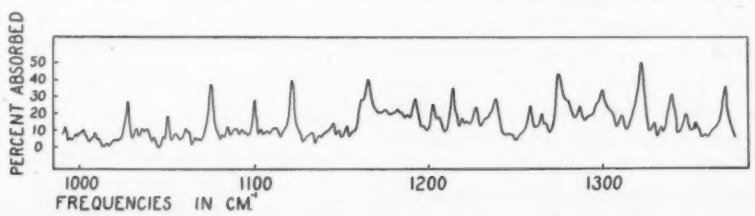

FIG. 2. The perpendicular absorption bands (ω_5:ω_6) and (ω_6:ω_3) showing the effect of Coriolis interaction.

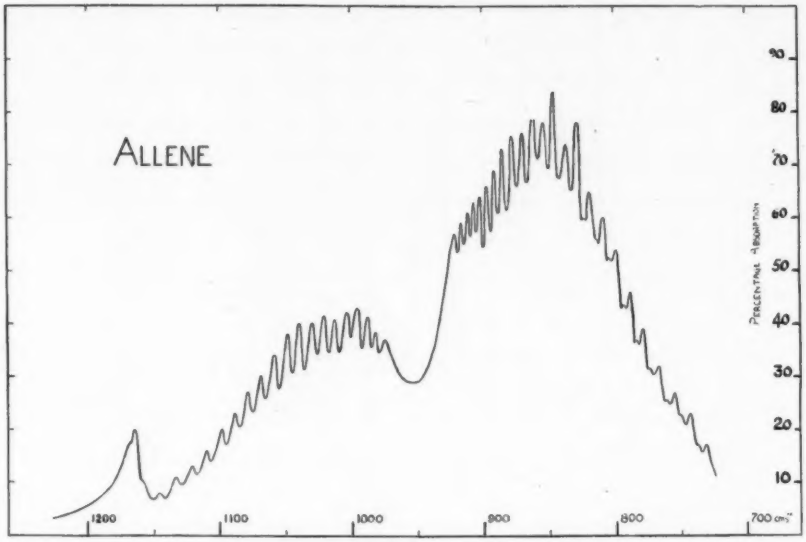

FIG. 3. Two perpendicular absorption bands in the spectrum of allene, measured by Dr. Harold W. Thompson of Oxford University, Oxford, England, showing the effect of Coriolis interaction.

contains the denominator $\omega_s^2-\omega_{s'}^2$ and when $\omega_s^2-\omega_{s'}^2$ is small this term may become by far the most important in the correction terms x_s, y_s, etc. This results in the band of higher frequency being degraded toward the red while the lower frequency band will be degraded toward the violet.

When $\omega_s \approx \omega_{s'}$ the contributions may actually become indefinitely large so that it becomes necessary to deal with the frequencies ω_s and $\omega_{s'}$ as degenerate and in such cases the non-diagonal elements $(v_{s'}, v_s, K|v_s\pm1, v_{s'}\mp1, K)$ of the term (6) become of first-order significance. Let us suppose the frequencies ω_s and $\omega_{s'}$ are associated with oscillations of the molecule directed, respectively, along the axis x and y, fixed in the molecule. The internal angular momentum p_s is therefore directed along the axis z and it will be coupled to the component of the total angular momentum P_z. We consider this case because it becomes of importance in many molecules of axial or approximate axial symmetry such as CH_3X, CH_2X, or $(CH_2)_2X$. In such instances the $(v_s, v_{s'}, K|v_s+1, v_{s'}-1, K)$ elements are found to be the following:

$$(v_s, v_{s'}, K|v_s+1, v_s-1, K) = i\zeta_{ss'}ZeK[(\omega_{s'}/\omega_s)^{\frac{1}{2}}+(\omega_s/\omega_{s'})^{\frac{1}{2}}]. \quad (7)$$

To obtain the energies one proceeds as before by diagonalizing the secular determinant which has the elements (1) and now also the non-diagonal elements (7). The diagonal elements (1) are altered to the extent that now all terms x_s, y_s, and z_s containing $(\omega_s-\omega_{s'})$ as a denominator are absent. In its place, however, will be a term proportional to $(\omega_s-\omega_{s'})$ which will be small.

We shall apply the above to the case of the two fundamental states of the frequencies ω_s and $\omega_{s'}$ (i.e., where $v_s=1$, $v_{s'}=0$; $v_s=0$, $v_{s'}=1$). For simplicity we shall assume the molecule to be symmetric so that we may set X_v-Y_v equal to zero. The secular determinant for the energies will then be the following:

$$\begin{vmatrix} x & & & \\ & x & (1,0) & (0,1) \\ & (1,0) & E_{1,0}/hc-W & i\zeta_{ss'}KZ_e[(\omega_s/\omega_{s'})^{\frac{1}{2}}+(\omega_{s'}+\omega_s)^{\frac{1}{2}}] \\ & (0,1) & -i\zeta_{ss'}KZ_e[(\omega_s/\omega_{s'})^{\frac{1}{2}}+(\omega_{s'}/\omega_s)^{\frac{1}{2}}] & E_{0,1}/hc-W \\ & & & & x \\ & & & & & x \end{vmatrix} = 0, \quad (8)$$

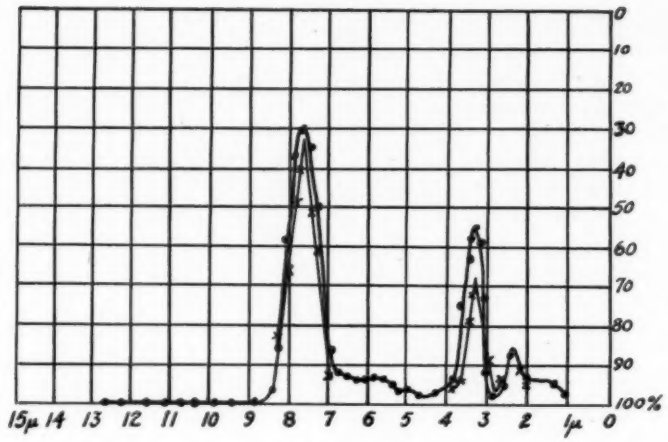

FIG. 4. The Spectrum of CH_4 in the infra-red showing an absorption maximum near 1500 cm^{-1} interpreted to be the forbidden transition ω_2.

where $E_{1,0}$ and $E_{0,1}$ are, respectively, the values of the diagonal elements where $v_s=0$, $v_{s'}=1$ and $v_s=1$, $v_{s'}=0$, all the other $v_{s''}$ being equal to zero. For all values of v except v_s and $v_{s'}$ the above secular determinant gives the roots which are exactly the same as the diagonal elements (1). For the roots corresponding to the two levels $v_s=0$, $v_{s'}=1$ and $v_s=1$, $v_{s'}=0$ we have:

$$W(\pm)=E(\pm)/hc=(1/2hc)\Big\{[E_{1,0}+E_{0,1}]$$
$$\pm\Big([E_{1,0}-E_{0,1}]^2+4\zeta_{ss'}^2K^2Z_e^2$$
$$\times\Big[\Big(\frac{\omega_s}{\omega_{s'}}\Big)^{\frac{1}{2}}+\Big(\frac{\omega_{s'}}{\omega_s}\Big)^{\frac{1}{2}}\Big]^2\Big)\Big\}^{\frac{1}{2}}+\sum_{s''}(\omega_{s''}/2). \quad (9)$$

The energy of the molecule in the normal state is evidently

$$(E(0)/hc)=\sum_s(\omega_s/2)$$
$$+[J(J+1)-K^2]X_e+K^2Z_e. \quad (10)$$

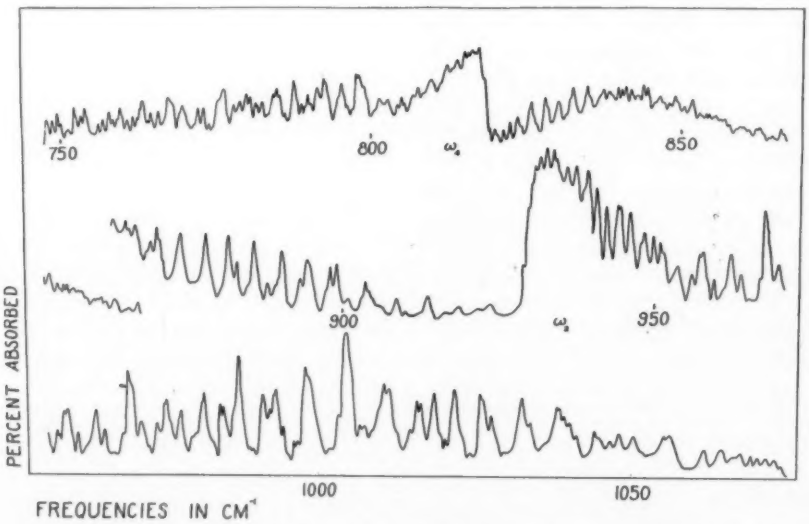

FIG. 5. Absorption bands in the spectrum of GeH_4 near 12μ. The more intense band is ω_4 and the other is the forbidden transition ω_2.

The bands (+) and (−) which occur when the molecule makes a transition from the normal state to the resonating levels $E(\pm)$ will be perpendicular bands (i.e., the electric moment induced will be normal to the body fixed axis z. The most important lines, for observational purposes, in such a band are due to the transitions $\Delta J=0$, $\Delta K=\pm 1$; especially if $Z_e \gg X_e$ as is the case in molecules like CH_2X, $(CH_2)_2X$, CH_3X, etc. If one makes the approximation that $X_v=X_e$, $Z_v=Z_e$ in all cases and observes the fact that the line frequencies are given by the Bohr frequency condition $\nu=(E(\pm)-E(0))/hc$ subject to the above selection rules, one obtains for the positions of the lines in these bands:

$$\nu=(\omega_s+\omega_{s'})/2-(Z_e-X_e)\pm\tfrac{1}{2}\{(\omega_s-\omega_{s'})^2 +4(K\zeta_{ss'}Z_e[(\omega_s/\omega_{s'})^{\frac{1}{2}}+(\omega_{s'}/\omega_s)^{\frac{1}{2}}])^2\}^{\frac{1}{2}} \pm 2K(Z_e-X_e), \quad (11)$$

where K takes the values 0, 1, 2$\cdots$. It will be seen that when $(\omega_s-\omega_{s'})$ is large compared to $K\zeta_{ss'}Z_e[(\omega_s/\omega_s)^{\frac{1}{2}}+(\omega_{s'}/\omega_s)^{\frac{1}{2}}]$ the spacing between two of these Q branches approaches the normal spacing $2(Z_e-X_e)$. As K increases the spacings approach a value.

$$\Delta\nu(\pm)=2\{(1\pm(\zeta_{ss'}/2)[(\omega_s/\omega_{s'})^{\frac{1}{2}} +(\omega_{s'}/\omega_s)^{\frac{1}{2}}])Z_e-X_e\}. \quad (12)$$

The above effect was first recognized in the two resonating bands ω_5 and ω_6 in the spectrum of formaldehyde[5] vapor shown in Fig. 2. It has since been observed in many other cases. Recently Dr. Harold W. Thompson of Oxford University in England has observed two such resonating perpendicular bands in allene $(CH_3)_2C$[6] which demonstrate the above effect more lucidly than in any previously known case. Dr. Thompson has most generously made this data available to the author for this paper. The data recorded by Thompson are shown in Fig. 3. These data were recorded on a prism spectrometer and the positions of the lines are not known to a very high accuracy. It is clearly seen from Table II, however, that the lines in the higher frequency band are degraded toward the violet. They appear to converge to a limiting value. $\Delta\nu(-)=5$ cm^{-1} and to diverge at the other extremity to a value $\Delta\nu(+)=12$ cm^{-1}.

TABLE II. Positions of Q branches, in wave-number units.

Band 845		Band 1030	
922	5	975	6
917	5	981	7
912	5	988	8
907	5	996	8
902	5	1004	9
897	6	1013	8
891	6	1021	9
885	7	1030	10
878	8	1040	9
870	8	1049	10
862	8	1059	10
854	8	1069	10
846	9	1079	10
837	9	1089	10
828	9	1099	11
819	10	1110	11
809	10	1121	12
799	11	1133	13
788	10	1146	12
778	11	1158	
767	12		
755	12		
743	12		
731			

Because of the perturbation there arises a "mixing" of the wave functions. The stabilized wave functions will be linear combinations of the unperturbed wave functions, the coefficients being the normalized first minors of the secular determinant for the energies. Because of this fact the intensities with which a transition will occur may be substantially altered—even to the extent that "forbidden" transitions may arise. The most notable example is the appearance of ω_2 in the spectrum of the tetrahedrally sym-

[5] E. S. Ebers and H. H. Nielsen, J. Chem. Phys. **5**, 822 (1937).
[6] Harold W. Thompson (private communication).

metric molecule. This frequency is essentially due to a motion of the four atoms at the corners of the tetrahedron on the surface of the sphere. Normally such a frequency would be inactive in the infra-red, but because of a Coriolis resonance interaction with the extremely intense fundamental ω_4, it becomes observable in the spectrum. The frequency ω_2 appears to have been observed by Coblentz[7] in the spectrum of CH_4. Coblentz's prism curve is shown in Fig. 4, which clearly shows an absorption maximum near 1500 cm^{-1}. This is known to be the approximate value of ω_2 for that molecule. In the case of the spectra of SiH_4 and GeH_4 these bands have been studied in considerable detail.[8] Figure 5 shows the region for GeH_4, the less intense band being ω_2. The same effect may be expected to prevail in the spectra of other molecules although it has not been observed elsewhere. Shaffer has shown in an unpublished work that one might expect the torsional oscillation in the molecule C_2H_4 to become observable because of an interaction of this type with a neighboring band.

It is of interest to note that first-order Coriolis resonance interactions are always due to resonance between two fundamental frequencies and never between fundamentals and overtones. Second-order Coriolis resonance interactions may also occur but these will arise only when resonance exists between fundamentals and combination frequencies. Their effect is probably small and will not be considered in this discussion.

It should be apparent from the foregoing that because of the anomalies which they give rise to in the spectra of polyatomic molecules a knowledge of the types of resonance interaction which may occur between vibration frequencies and which may contribute to the energy in first or second order is important in arriving at an understanding of the structure of the molecule from which the spectra originate.

[7] W. W. Coblentz, *Investigations of Infrared Spectra* (Carnegie Institution of Washington, 1905), Part I, p. 166.
[8] W. H. Shaffer (private communication).

JOURNAL OF THE OPTICAL SOCIETY OF AMERICA VOLUME 34, NUMBER 9 SEPTEMBER, 1944

A Calculation of Newton Ring Tolerances for Prism Faces

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(Received February 25, 1944)

IF the incident beam of light on an optically homogeneous prism is composed of parallel rays, and the polished faces of the prism are truly plano, it may be assumed that the emergent beam will be composed of parallel rays. Thus, with a good collimator, and a prism made of well-annealed optical glass, any angle between emergent rays (relative deviation) may be attributed to the imperfect figure of one or more of the prism faces.

In this paper only one type of prism is considered: the 90°–45°–45° with three polished faces. The Porro prisms commonly used in binoculars are of this type.

I have chosen for the calculation a prism which is set in an instrument in such a way (Fig. 1) that the incident beam enters one of the short faces (or legs) at 45°, is reflected inside the prism at the hypotenuse face, and emerges, supposedly parallel to the original beam, through the other short face.

The head prisms and erector prisms in the Navy's Mk. 60 telescope are used in this way. For these prisms the rays of the emergent beam must be parallel to within three seconds. This is the tolerance assumed in the sample calculation shown here.

The problem is to determine the allowable error for the prism faces which will correspond to 3″ maximum relative deviation. This tolerance, expressed in Newton rings, will be the limits within which the optical shop must work.

In the sample calculation several special assumptions are made: (1) that the two short faces are truly plano; (2) that the hypotenuse face is a convex, circular-cylindrical surface, whose longitudinal axis is parallel to each of the two short faces (i.e., no pyramidal error); and (3) that an imaginary plano hypotenuse, constructed parallel to the longitudinal axis of the cylindrical surface, will make an angle of 45° with each of the two short faces (i.e., the two short faces are the same length). In other words, the center of curvature of the cylindrical surface lies on an extension of the vertical axis of symmetry (which bisects the 90° angle) of the prism.

The effect of these assumptions on the general method, and on the final result, is discussed at the end of the paper.

In a perfect prism (Fig. 1), every ray forms two similar triangles within the prism. (The two 45° angles of the prism are equal, and the angle of incidence at the hypotenuse equals the angle of reflection.) Thus, $90°+r_1=90°+i_2$, and since the prism has air on both sides, $i_1=r_2$.

We see (Fig. 2) that i_1 and r_1 remain unchanged. Thus,

$$N=\sin i_1/\sin r_1. \tag{1}$$

For sodium light, using Bausch & Lomb's borosilicate crown glass (BSC-2), $N=N_D=1.5170$. Since the prism is oriented with respect to a collimator, which furnishes parallel light, $i_1=45°$. This gives $\sin r_1$ directly.

Figure 2 shows three rays; the outside two represent the extreme rays, making an angle of 3″ between them. The center ray is not used in the calculations. The outside rays are considered as being reflected at the corners of the prism, but for clarity in the drawing they are represented slightly in along the hypotenuse.

At the curved hypotenuse, the normal is turned θ degrees (compared to Fig. 1). θ is the angle subtended at the center of curvature by half the hypotenuse. For the upper (x) ray, the angle of reflection is decreased by θ; for the lower (y) ray, the angle of reflection is increased by θ. Thus, at the emergent face,

$$N=\sin x/\sin (r_1-\theta) \tag{2}$$

and

$$N=\sin y/\sin (r_1+\theta), \tag{3}$$

where x and y are the angles of refraction at the emergent face.

From the specifications we have,

$$(r_2-x)+(y-r_2)=3''. \tag{4}$$

Three more equations are needed to complete the calculation.

$$\sin\theta=\frac{(\text{hyp./2})}{R}=\text{hyp./}2R, \qquad (5)$$

where R is the radius of the cylinder, and hyp. is the length of the imaginary plano hypotenuse, the distance between the corners of the prism.

Using the accurate sagitta formula,

$$S=R-(R^2-\text{hyp.}^2/4)^{\frac{1}{2}}, \qquad (6)$$

where S is the sagitta of the cylindrical surface.

The number of Newton rings, when starting from zero thickness, equals twice the number of times the wave-length is contained in the maximum optical retardation.[1] Thus,[2]

$$\text{number of rings}=2N_{\text{air}}\,S\cos i/\lambda.$$

We regard $N_{\text{air}}=1$, especially since we used the index of refraction of the glass as measured in air. We count rings when looking at them normally, so $\cos i=1$. We use sodium light, so $\lambda=\lambda_D=5893\text{A}=0.0005893$ mm. Thus,

$$\text{number of rings}=2S/.0005893. \qquad (7)$$

COMPUTATION

We want to compute $\sin\theta$. Substituting trigonometric identities into Eq. (3) and Eq. (2),

$$\sin y=N\sin r_1\cos\theta+N\cos r_1\sin\theta, \qquad (3a)$$
$$\sin x=N\sin r_1\cos\theta-N\cos r_1\sin\theta. \qquad (2a)$$

Substituting Eq. (4) into an identity,

$$\sin y=\sin(x+3'')=\sin x\cos 3''+\cos x\sin 3''. \qquad (4a)$$

We have four known constants: $K_1\equiv N\sin r_1$; $K_2\equiv N\cos r_1$; $K_3\equiv\sin 3''$; and $\cos 3''=1$, to more than six decimal places.

Substituting the constants, combining Eq. (3a), Eq. (2a), and Eq. (4a), and simplifying, we get

$$(4K_2^2/K_3^2)\sin^2\theta=1-\sin^2 x.$$

Let $K_4\equiv 4K_2^2/K_3^2$. We continue expanding squares, eliminating $\cos\theta$ by substitutions of $(1-\sin^2\theta)^{\frac{1}{2}}$, and simplifying. We end up with

$$\sin^2\theta=\frac{K_8\pm(K_8^2-4K_7K_6^2)^{\frac{1}{2}}}{2K_7},$$

where $K_8\equiv 2K_5K_6+4K_1^2K_2^2$; $K_7\equiv K_5^2+4K_1^2K_2^2$; $K_6\equiv 1-K_1^2$; and $K_5\equiv K_4+K_2^2-K_1^2$.

Substituting numerical values, K_4 turns out to be a big number, $\log K_4=10.532252$. Since K_1 and K_2 are each approximately unity, K_5 does not differ from K_4 within the six decimal places we are using. $K_1\equiv N\sin r_1=\sin i=\sin 45°=\frac{1}{2}^{\frac{1}{2}}$; thus, $K_6=0.5$. K_7 reduces to K_8^2 which reduces to K_4^2. K_8 reduces to K_4 also. This reduces the radicand to zero, so that $\sin^2\theta=K_8/2K_7$, which reduces to $\sin^2\theta=\frac{1}{2}K_4$. This, in turn, gives

$$\sin^2\theta=\frac{\sin^2 3''}{8N^2\cos^2 r_1}.$$

Combining this result with Eq. (5), Eq. (6), and Eq. (7), we get,

$$\text{number of rings}=\frac{\text{hyp.}\,[8^{\frac{1}{2}}N\cos r_1-(8N^2\cos^2 r_1-\sin^2 3'')^{\frac{1}{2}}]}{\lambda\sin 3''}.$$

This expression, however, is not suitable for making calculations, because the numerator is obtained as the difference between two very nearly equal numbers. Instead, after using Eq. (5), we are obliged to write Eq. (6) in the form

$$S=\frac{(\text{hyp.}^2/4)}{2R-S}$$

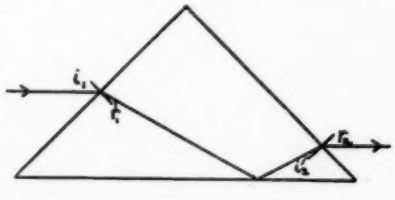

FIG. 1.

[1] We need not be concerned here with the 180° phase change, which is due to one of the reflections taking place in a rare medium against a dense medium. The accepted procedure in the optical shop is to count the Newton rings out from the center of the pattern, counting only those that have the same color as the "bull's eye." Thus, for a maximum air-space thickness less than 10^{-5} mm (and yet not in optical contact) we observe no change from the center out, and so although from our theory we know that there is actually interference taking place, we say there are zero rings ("all one color").

[2] G. S. Monk, *Light, Principles and Experiments* (McGraw-Hill Book Company, Inc., New York, 1937), p. 140.

which can be solved by successive approximations. In the given case, where hyp. was 74.39 mm, only two substitutions were necessary. R is found to equal 9,707,990 mm; the sagitta equals 0.00007 mm; and the number of rings equals 0.24.

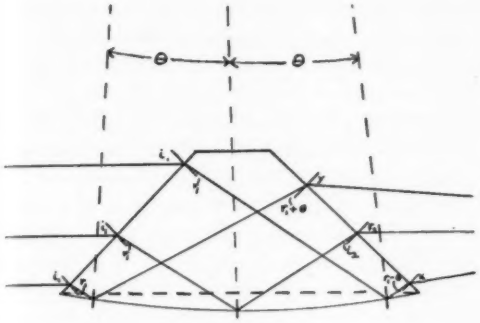

FIG. 2.

CONCLUSIONS

The first of the three special assumptions, that the two short faces are truly plano, means that the result computed is approximately three times too large, if we consider that all three surfaces are convex and that the errors, therefore, are cumulative. We should not assume this, of course, any more than we should assume that the errors will cancel each other out. The computation indicates, more or less, the maximum allowable algebraic sum of the three errors, a practical tolerance to specify. If the prism did not have to be quite so accurate, however, it would be advisable to tighten the computed tolerance a little.

The second assumption was introduced to simplify the problem. We could have assumed a spherical surface and considered Fig. 2 the cross section through the center of the prism. Then, using the width of the hypotenuse instead of the length in Eq. (5) and Eq. (6), we could have computed the Newton ring tolerance across the hypotenuse. Assuming a regular form (cylinder or sphere) to the error of figure, however, does not affect the accuracy or generality of the result. Assuming no pyramidal error does not affect the accuracy either, because pyramidal error enters only as a higher order correction.

The third assumption means that the prism is considered to have no angular error. A prism used in this position does not depend at all on the accuracy of the 90° angle to render the emergent rays parallel to the incident rays, but only on the *equality* of the acute angles. Any inequality of the acute angles, however, will not introduce *relative* deviation (between rays on the emergent side of the prism), but will only affect the total deviation. Thus, unequal acute angles do not prevent orientation of the prism with respect to the collimator so that the emergent rays are parallel to the incident rays.

If the maximum allowable relative deviation is fairly large, the approximations introduced into the calculations are no longer justified. The $\cos 3' = 1$ to six decimal places, but not to seven.

It is not necessary, however, to use six-place tables. If five-place tables are used (λ is given to four significant figures; N_D is given to five; the hypotenuse length to four; the number of Newton rings is needed only to two significant figures), the method shown is sufficiently accurate up to a relative deviation of half a degree.

Reducing Electrical Interference from Spectrographic Spark Source

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(Received June 2, 1944)

RECENTLY a problem of electrical interference was called to the attention of the writer and its solution warrants mention. A vacuum photoelectric cell and amplifier are used to measure the photographic density of the

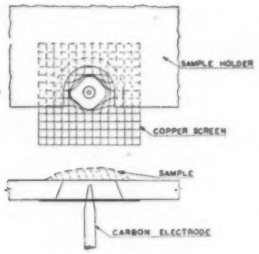

FIG. 1.

spectral lines. The interrupted high voltage spark made so much disturbance in the densitometer that it was impractical to use both at the same time; thus the efficiency of the spectrographic laboratory was reduced. The high voltage (35,000 volts) interrupted spark operates into a capacity of 0.007, 0.014, or 0.021 microfarad and an inductance of 0.04, 0.08, 0.16, or 0.32 millihenry connected in series with the spark gap. Insulated leads about fifteen feet long conduct the high frequency current to the spark stand. The manufacturer recommends substantial ground connections and, if this fails to remedy the condition, the separation of the densitometer from the spectrograph by a certain distance. The physical dimensions of the laboratory, as is often the case, made it impossible to separate further the two units. Therefore, other means of eliminating this disturbance were sought.

The conventional methods of reducing interference were tried by grounding component parts using special ground rods, shielding electrical conductors carrying high frequency currents, and almost completely shielding the spark stand itself. None of these eliminated the difficulty. However, these tests did show a decrease in the irregularity of the galvanometer deflection. Heavy sheet iron squares placed between the spark electrodes and densitometer produced little if any effect. It was interesting to find that a number of people standing about the densitometer greatly reduced the erratic deflection.

Since the resonant circuit in the spark source has a natural frequency of approximately 100 kc, depending of course on the value of capacitance and inductance, this could hardly cause such disturbance when the shielding was considered. Therefore, a much higher frequency must be involved which emanates from the electrodes and is reflected about the room, finally reaching the photoelectric cell and amplifier circuit.

Upon the writer's suggestion, Mr. Emil Prandoni placed a screen gauze just below the sample holder, shown diagrammatically in Fig. 1. The erratic galvanometer deflections ceased almost completely. He also tried a solid copper ring about the $\frac{1}{4}$-inch carbon electrode, Fig. 2, and found this to be equally effective. This ring may be attached to the sample holder. It occurs

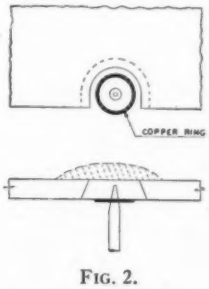

FIG. 2.

to the author that other laboratories have also experienced this difficulty and would find this simple remedy valuable. The shield is easily applied and seems to be very successful. Experimentation will indicate the proper position.

Brightness* Constancy in Photographic Reproductions**

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(Received July 21, 1944)

I. INTRODUCTION

ONE of the basic relations in photographic theory is that which exists between the exposure to which a material is subjected and the result which is produced from this exposure by the subsequent operations of developing and printing. This relationship has been given exhaustive study for many years. The fundamental work of Hurter and Driffield and of Renwick, Jones, and others[1] has established a series of principles known as the "theory of tone reproduction." In brief, these principles state that if the photographic material is properly developed and printed, it is theoretically possible to obtain a print in which every point of the subject is so reproduced that the relative reflectances of any two points of the print are in the same ratio as the intensities of the light received from the corresponding points of the subject. This condition is specified in photographic theory by the statement that the exposures be on the straight-line portion of the over-all response curve of the negative and the print, and that the over-all gamma be unity. Under these conditions, the ratio of any two luminances in the subject will exactly correspond to the ratio of the reflectances and hence luminances of the corresponding points of the theoretical print. (The photographic material is here assumed to have the same color sensitivity distribution as the eye.) This relation therefore deals with the intensity of the light reflected from the object as evaluated by the eye of a standard observer (luminance) and its relation to the reflectance of the corresponding point of the reproduction. In uniform illumination, the reflectance of an area determines its luminance relative to any other area in the same illumination. In this way, it is seen that the relative luminances of the print become identical with the relative luminances of the subject.

It is recognized by the specialists in the field of tone reproduction that such a physical identity of the luminance ratios is a solution only of the objective phase of tone reproduction. It is unfortunately true that many popular writers on the subject also assume that the existence of such a relation is all that is necessary to make the print have the same appearance as the original scene.

Several factors tending to make the print appear different from the actual scene have been discussed by Evans[2] in a previous paper. He pointed out that, in general, the relationship does not lead to the correct appearance when the illumination of the scene is non-uniform. It is the purpose of the present paper to present the results of an experimental study of this problem in relation to a simple type of portrait lighting.

We have first to consider somewhat more closely the relationship between the luminances of the scene itself and their perceived brightnesses. This subject has received much attention from psychologists (see, for example, the work of Katz, Thouless, MacLeod, and others). Briefly summarized, their conclusions may be stated as follows: If the illuminance falling on a scene is everywhere the same, then there is what might be called a 1-to-1 relation between luminance and brightness. (This relation, of course, is between the logarithm of the luminance and the brightness and holds only at photopic levels.) The highest luminance in the scene is the highest brightness, and the lowest is the least bright. All intermediate luminances fall in the same order between these two, as do the perceived brightnesses. The reflectances, therefore, since they control the luminances, also fall in the same order and stand in the same relation to brightness.

When the illumination is non-uniform, how-

* In this paper, the recent nomenclature given in the "Report of the Colorimetry Committee of the Optical Society of America," published in the J. Opt. Soc. Am. **33**, 544 (1943), is used; i.e., "brightness" is the word applied to the subjective perception of radiant energy, while "luminance" is the psychophysical evaluation of it with respect to the standard observer.

** Communication No. 975 from the Kodak Research Laboratories.

[1] See, for example, C. E. K. Mees, *Theory of the Photographic Process* (The Macmillan Company, New York, 1942), Chapter XX, pp. 755–831.

[2] R. M. Evans, J. Opt. Soc. Am. **33**, 579 (1943).

ever, no such simple relationship is found. Under these conditions, a new phenomenon appears which is known among psychologists as "approximate brightness constancy" (in the new nomenclature it should be called "approximate lightness constancy"). This phenomenon consists of a visual separation between the apparent luminance ("brightness") of a given area and its apparent reflectance ("lightness"). That is, the two properties of the particular area of the subject toward which the attention is directed tend to be perceived as independent of each other. It is further found that the tendency is to perceive them both more nearly as they would be in uniform illumination. Thus, an object in shadow will be perceived as having a somewhat higher luminance than it actually has but at the same time will appear to have a reflectance of very nearly its true value, even though the actual *luminance* is far below that of a lower *reflectance* in high *illuminance*. The net result of this confusing state is a complete disappearance of any simple relation between luminance and brightness, on the one hand, and reflectance and lightness, on the other. The observer *tends* to see them in their correct values but does not do so in the majority of cases. Brightness no longer correlates at all with reflectance.

A numerical example may make the phenomenon clearer. Suppose a surface with a reflectance of 20 percent stands in an illuminance of 20 lumens per square foot, while a surface with a reflectance of 50 percent stands in a shadow where the illuminance is 2 lumens per square foot. The luminances of the two surfaces are 4 foot-lamberts per square foot and 1 foot-lambert, respectively. A trained observer compares these two areas with a group of reflectances in uniform illumination in the foreground. He finds that the surface in the shadow appears to have a reflectance of 40 percent, while that in full illumination is perceived correctly at 20 percent. The area in the shadow thus looks lighter to him than the area in full light. When he judges their brightnesses, however, he judges that the area in shadow has half the luminance of the area in the full light. It is perceived, therefore, as less bright, but its true luminance is overestimated. This is the usual situation with objects in shadow or in a region of decreased illumination, but the effect is frequently of much greater magnitude than implied by the example. In extreme cases, an area which appears black may have a higher luminance than another which is perceived as white.

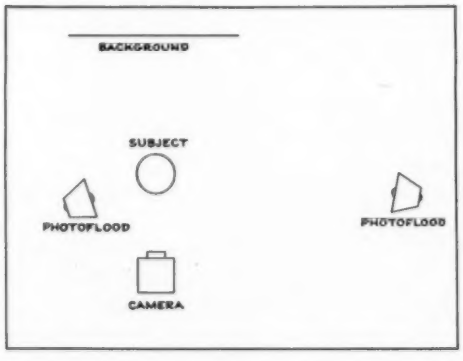

FIG. 1. Lighting diagram for the visual effect desired.

The photographic process, when correctly used, is capable of a correct reproduction of all the relative *luminances* of the scene. In general, however, as was pointed out in the previous article,[2] the brightnesses and lightnesses of a non-uniformly lighted scene are not perceived the same in such a print as in the scene itself. It was shown, furthermore, that this was due not to the *absence* of the brightness constancy effect but to a relatively severe decrease in its magnitude, the extent of the loss varying greatly with the subject matter of the picture. It was noted that this loss of effect could be offset by a change in the lighting of the subject.

The purpose of the present investigation was to determine for a simple case just what these changes had to be. It was hoped that in this way it would be possible both to clarify the nature of the effect further and to learn some of the restrictions which it places on the photographic process.

II. EXPERIMENTAL

As a simple subject, a plaster of Paris bust, uniformly colored in light ivory, was chosen. This was placed some distance in front of a gray background and illuminated from both sides by two Photoflood lamps in the positions shown in Fig. 1. The luminances of the two sides of the face were measured with a Macbeth illuminometer

FIG. 2. Photograph obtained with lighting of Fig. 1.

and found to have a ratio of 8 to 1. It was decided to attempt to obtain a photographic print which, when viewed under uniform illumination, would appear as nearly as possible as the subject appeared under these conditions.

The picture, which was obtained by a direct photograph following the principles of tone reproduction, is shown in Fig. 2.

In the photographic print from which the reproduction was made, the reflectances of the two sides of the face had a ratio of 8 to 1 in accordance with the luminances of the subject. The appearance of the print, however, bore little resemblance to the appearance of the subject. The subject did not appear much darker on the low illuminance side than on the other, and the background appeared gray and not black.

Two major differences between the reproduction and the subject, then, were obvious at this point. The lighting contrast had been greatly increased, and the background had been very materially darkened, in spite of the fact that the print did have the same relative luminances as the subject.

Since the right side of the face appeared too dark, it was necessary to move the right-hand lamp closer to the subject and take a series of pictures until the *brightnesses* of the two sides appeared in the print as in the subject. This series showed that, for this particular set-up, the measured luminances had to be reduced to a ratio of about 2 to 1 to produce this effect. The background was still too dark, and the bust itself still appeared to be more contrasty in the print than in the original set-up. A study of the print by direct comparison showed that this contrasty effect was produced by the shadows cast by the contours of the figure. Wherever a shadow was cast, it was much too dark.

FIG. 3. Lighting of Fig. 1 but figured background.

For a reason to be discussed presently, it was decided that a figured background should be substituted for the dark gray. The lights were returned to their original positions (as in Fig. 1), and the photograph shown in Fig. 3 was obtained.

FIG. 4. Background separately illuminated.

FIG. 5. Lighting of Fig. 4 but with low over-all gamma.

Two lights were then added to illuminate the background separately until photographs showed that the relative brightnesses of the background and the bust were the same in the print as they had been in the subject. It was found that the illuminance required was the same as that of the high illuminance side of the face. The photograph obtained with this added illuminance is shown in Fig. 4.

With the brightness of the background raised to the proper level, consideration was next given to the reduction of the contour shadow contrasts. Two possibilities suggested themselves. The contrast of the whole reproduction could be decreased by a change of the gamma of the photographic process, or the contrasts could be decreased by the addition of further light directed into the shadows.

Since the addition of still more lights seemed undesirable if it could be avoided, a series of pictures was made, each at a different gamma lower than 1. A study of these pictures showed that *as far as the bust itself was concerned* it was, indeed, possible to obtain a reproduction which had the same brightness contrast as the original subject. The best print (over-all gamma about 0.4) is shown in Fig. 5.

This picture, however, shows two very important and noticeable defects. Wherever there is detail visible in *uniform* illumination, as there is in the background and in the large areas in shadow, the contrast is now much too low, although the sides of the face do have the proper contrast. In addition to this, the modeling of the figure has been reduced over the appearance of the subject itself. It was because of the expectation that the first of these defects would appear as soon as any departure was made from the principles of tone reproduction that the figured background in uniform illumination was added originally. The bust itself is an object of *uniform reflectance* in non-uniform illumination and hence represents an oversimplified case. With the figured background, the more usual case of non-uniform reflectance is introduced, and the defect

shows up immediately, as it would in the case of a person sitting for a portrait.

The problem now became one of reducing the shadow contrasts and decreasing the side-to-side illumination ratio simultaneously while retaining the added light on the background and maintaining the photographic process at a gamma of unity. This was accomplished by the addition of a single lamp beside the camera, which threw light into all the visible shadows but did not itself form shadows which were visible from the camera. After a series of trials, it was found that the proper shadow illuminance was about twenty times the former value. Keeping this front light constant, the right-hand lamp was then moved in until the luminances of the two sides of the face had the previously chosen ratio of 2 to 1. This lamp position, of course, was not as close to the bust as before, since some contribution was made to the illuminance of this side of the face by the front light.

Under these lighting conditions, a picture was obtained which was considered acceptable in direct comparison with the subject illuminated as shown in Fig. 1. The print is reproduced in Fig. 6, and the positions of the lights for this picture are shown in Fig. 7. (It should be pointed out that the limitations of the halftone process have tended to minimize the differences in these figures. It is hoped, however, that the principles involved will be sufficiently apparent.)

In the course of making the prints for this series of experiments, one other factor determining the fidelity of the reproduction became apparent. The negatives for all the lighting conditions were so exposed that all the densities fell on the straight-line portions of the characteristic curves of the negative material.

At first, no proper criterion seemed available to obtain the best print from the standpoint of the present work, and long series of prints were made from which the one *most nearly* approaching the appearance of the subject was chosen. It soon became obvious from the series that the best print in each was that in which the *reflectance* of the more brightly lighted side of the bust in the print *matched* the *reflectance* of the bust itself. This was due to the presence of the white border on the print, which acted as a fixed reference standard for white. Lighter prints made the material of the bust look too white and darker ones too gray.

This conclusion raised the question as to whether or not a difference in the simultaneous contrast effects in the print as compared to the subject might be playing a large part in the results. Because of the inherent interest in simultaneous contrast as a possible factor in brightness constancy itself, and to see what effect extreme background differences would have on the required print density, a further series of tests was undertaken. There are four possible cases of extreme background contrasts for this particular subject: The background may be all white or all black, or it may be divided down the center with black or white on either side.

FIG. 6. Front light added and side light adjusted.

A series of identical prints was cut out around the figure and mounted on these four types of background. The figures with the divided backgrounds are reproduced as Figs. 8 and 9. They show that the maximum effect on brightness

constancy which can be produced by a change in the background of the figure is very small compared with the change in illumination which is necessary for correct lighting.

The pair with the white and black backgrounds showed that in order for the bust to appear to have its correct reflectance, the one on black must be darker and the one on white lighter than with the figured background. Any difference in simultaneous contrast effect between the subject and its reproduction must, therefore, be compensated by a suitable adjustment of the print density. In the absence of such a *difference*, the true reflectance is the proper value for the print.

III. DISCUSSION

Those with experience in portrait photography will recognize at once that the customary lighting system used by the majority of portrait photographers has here been built up, step by step. Each step has been *necessary* to make the picture look like the subject. It remains to consider why each was necessary. In doing this, it would be desirable to refer the results to a theory of brightness constancy. Unfortunately, no adequate and completely accepted theory appears to exist. The phenomenon occurs whenever a scene is *obviously* non-uniformly lighted (this is a

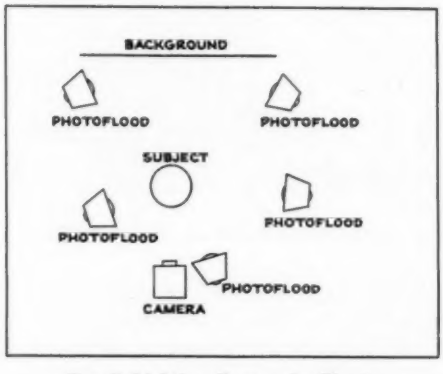

FIG. 7. Lighting diagram for Fig. 6.

sufficient, not a *necessary* condition), and it always acts to *decrease* the apparent non-uniformity.

As was pointed out, photographs do not show the absence of the effect but only a decrease in its magnitude. The amount of this decrease varies from a very slight loss to almost complete absence, two factors apparently controlling the decrease in any given case. These factors are the extent to which the objects are seen in relation to each other within areas of uniform illumination and the extent to which the type of illumination is apparent from the picture. It is, accordingly, different for every scene, for every type of illumination, and varies within the scene itself.

The experiments described may be analyzed from this point of view. In the first place, it was found necessary to increase the side illumination greatly to make the two sides of the face look correct. Since there was nothing whatever in the picture to indicate the nature of intensity of this side light, it may be assumed that this is a measure of the change made necessary by almost complete absence of any constancy in the print in this respect. It was next found necessary to illuminate the background to the full intensity of the strongest light falling on the bust. In this case again, since the background is not seen in comparison to other objects at the *same* intensity level as itself (and there is no way of knowing how far it lies *behind* the bust or how far from the light), almost no constancy effect is present in the photograph. Within the boundaries of the bust itself, however, the various areas are at different distances from the lights. The shading and modeling thus produced are simply exaggerated by the decrease in the constancy effect as compared to that occurring in the appearance of the original. To correct this, enough front lighting is needed to make up the deficiency.

This analysis indicates a number of important facts. Taken together, they define the problem of proper lighting for photography. Perhaps the first of these is that every scene will require different treatment to obtain the desired result. In some cases, much side lighting must be used, in others much front lighting. No definite rules can be laid down, since the proper ratios are determined by the extent to which "constancy" effects are produced by the picture compared to those present in the subject. A second fact is that all unrelated backgrounds must be independently illuminated to a level comparable to that of the main objects in the picture.

Another statement which might be justified is that if two lights only are to be used, placing a

front light beside the camera and a brighter light at one side is most likely to produce the best results.

These conclusions may all be summarized by saying that for almost any subject the lighting

FIG. 8. Background contrast aiding brightness constancy.

must be so arranged that the *lighting contrast* of the scene as viewed by the eye is very much less in *all* respects than is desired in the final picture. This obviously is the meaning of the term "flat lighting" as recommended for many years by manufacturers of photographic materials. It should be noted that this lighting cannot be produced with a single light except where this is beside the camera lens, and this fails completely if there are objects at various distances. "Flat" lighting is not produced by the sun unless the sun is directly behind the camera, in which case the shadow of the camera falls on the object being photographed. In professional exterior photography, flat lighting from sunlight is produced by reflecting the sunlight into the shadows or by the use of auxiliary lights, such as Photoflash bulbs.

From the standpoint of the photographic process, the results show that an over-all gamma of unity is the best condition, since uniformly illuminated detail is reproduced correctly only at this condition. In this respect, the work is a striking confirmation of the correctness of theory. In spite of the fact that many densities may be present in a print which do not appear in the same brightness relation as they do in the subject, an over-all gamma which reproduces *detail* correctly is still the *best* photographic result for the given lighting.

Finally, the only remaining variable, namely, the print density, is found to be specified by the appearance of reflectance of the main object. This appearance (lightness) is affected by back-

FIG. 9. Background contrast opposing brightness constancy.

grounds but is determined mainly by the presence of the white border.

IV. SUMMARY

An experimental study of the problem of photographing a simple scene showing the

"brightness constancy" phenomenon supports the following statements:

1. All objects in the picture whose illumination is not visibly related to that of the main object must be lighted to nearly the same illuminance as the main object.

2. The illuminance in shadowed portions of the main object must be greatly increased.

3. The gradation of illuminance from the main source of light must be decreased by auxiliary lighting.

4. Distortion of the tone reproduction scale cannot, in the general case, compensate for loss in the brightness constancy effect.

5. The density of the print must be so adjusted that the main object appears to have the correct reflectance. With a white border and no simultaneous contrast effects between object and background, this occurs when the lightest part of the main object in the reproduction ("catch lights" excepted) has the same reflectance as that of the object photographed.

JOURNAL OF THE OPTICAL SOCIETY OF AMERICA VOLUME 34, NUMBER 9 SEPTEMBER, 1944

An Arc Source for Ultraviolet Absorption Spectroscopy

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(Received February 25, 1944)

AN ideal source of radiation for ultraviolet absorption spectrophotometry by means of the photographic technique employing a rotating sector, "Spekker" photometer, notched Echelon cells, etc., with a quartz spectrograph would possess certain characteristics including: (a) high intrinsic brightness; (b) continuous spectrum; (c) freedom from fluctuations; (d) uniform intensity over its entire area; and (e) convenience of operation, requiring only simple accessories.

Light sources actually used for absorption studies are composite compromises of these five desirable characteristics. The hydrogen discharge tubes yield a spectrum nearly continuous from 200 mμ to 350 mμ but are of low intrinsic brightness, require considerable extra equipment, and are short-lived. In addition, stroboscopic effects and unequal distribution of illumination along the capillary may be sources of error unless a device to equalize the intensity through both solvent and solution cells, such as the Hilger rocking mirror, is employed.

The condensed underwater spark has been used by some investigators, but is troublesome to operate and requires elaborate equipment. The spark spectrum from uranium electrodes is sufficiently rich in lines so that for most purposes a continuous spectrum is obtained, but the uranium electrodes are expensive. The condensed spark between tungsten electrodes has been, probably, the most popular source for absorption spectroscopy and for most purposes is quite satisfactory. However, the line spectrum from this source is not entirely continuous; therefore, detection of fine structure of a complex absorption spectrum, and occasionally very accurate "spotting" of the match points to determine the exact positions of an absorption band maximum or minimum, are impossible. A number of d.c. arc sources have been tried but the wandering of the arc, the non-uniformity along the height of the arc column, and the great rapidity of the consumption of electrode materials have been sufficient causes for abandoning attempts to adopt the d.c. arc as a source of light for absorption studies.

As war conditions unavoidably delayed procurement of a spark generator for use with tungsten-steel electrodes, attention was given to other possible light sources. As a result of these trials, a modification of a source usually employed in emission analysis has been used for absorption experiments in this laboratory for over a year with entirely satisfactory results.

The source is the high voltage alternating

* This is one of four regional research laboratories operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

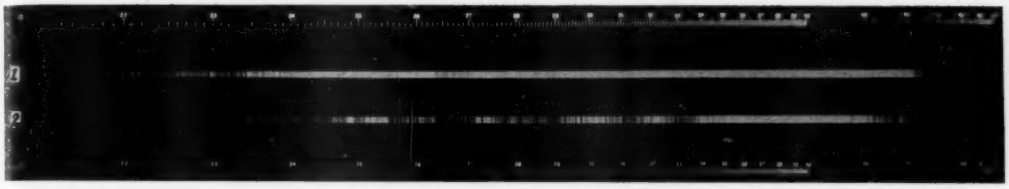

FIG. 1. Spectrograms of high voltage alternating current source with Hilger Spekker: *1*, 90-sec. exposure; *2*, 10-sec. exposure.

current arc recommended by Duffendack and Wolfe[1,2] for emission analysis, but impregnated carbon electrodes are used. The power is supplied by a pole transformer wired, in reverse to the usual practice, to step up the line voltage of 200 to 2400 volts. Inductance only is used to control the current. A single inductance tapped at appropriate points permits a ready choice of currents of 3, 3.5, 5.5, and 6.5 amperes, by manipulation of the proper single throw switch. When experimenting with this light source for absorption work, National Carbon Company therapeutic Carbon "B" was used as the electrode material, since previous experience had indicated that in the high voltage a.c. arc these rods burn steadily and relatively slowly. Subsequent studies with the Spekker photometer proved that when proper alignment had been attained, the high voltage a.c. arc was a very satisfactory source for absorption studies. One precaution should be noted. The electrode gap must be sufficiently large so that light (temperature radiation) from the rods themselves will be screened from the absorption cells by the Spekker stand. This necessitates a gap somewhat greater than that customarily used in emission analysis and careful maintenance of its exact position. The arc column is very stable and emission from the central portion is very uniform. The rate of consumption of the rods is more rapid than in the case of the condensed spark, but sufficiently slow that in some cases adjustment is necessary only after a series of exposures, particularly at the shorter exposure times with the photometer drum set for the lower density readings. When the higher density readings are being used, an adjustment, which can be rapidly accomplished, must be made after each exposure. The rapid rate of consumption and the ensuing need for continual readjustment of the rods are the chief disadvantages of this arc source.

Figure 1 shows spectrograms of the National Carbon Company, Therapeutic Carbon "B" source photographed with the Hilger Spekker. The photograph shows the uniformity of intensity through the solvent and solution cells when both are empty. Figure 2 is an example of an absorption curve obtained with the arc source.

[1] O. S. Duffendack and R. A. Wolfe, *Proceedings of the Fifth Summer Conference on Spectroscopy and Its Application* (John Wiley & Sons, Inc., New York, 1938).

[2] O. S. Duffendack and R. A. Wolfe, Ind. Eng. Chem. Anal. Ed. **5**, 226 (1933).

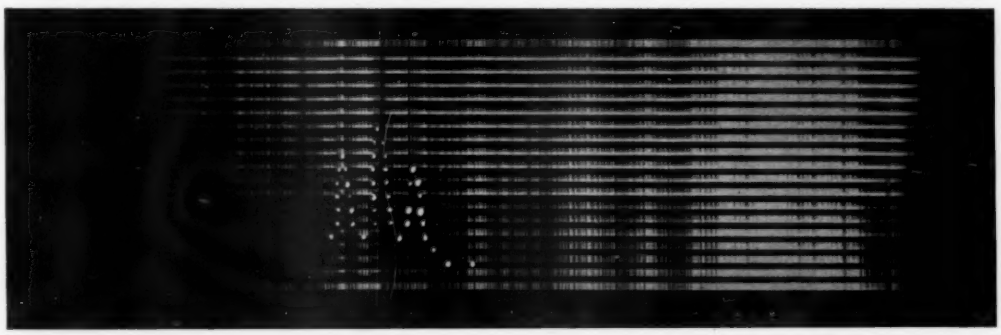

FIG. 2. Spectrogram showing absorption of benzene (in cyclohexane) photographed by means of arc source.

The spectrogram is the absorption curve of benzene, used to calibrate the instrument.

The high voltage a.c. arc has proved to be a satisfactory source for absorption studies of compounds isolated from commodities being studied in this laboratory. It uses no equipment not usually available in the spectrographic laboratory for emission analyses; it possesses the qualifications of being steady, uniform, and having sufficiently high intrinsic brightness. A complete absorption curve through the spectral range 2300A to 4000A can be photographed in about twenty minutes with density values varying from 0.0 to 1.5, and individual exposures, adjusted to maintain constant actinic values, varying from 5 seconds to 2.5 minutes. For measurements below 2300A, exposures varying from 15 seconds to 7.5 minutes are required. The use of Carbon "B" rods provides a spectrum of iron lines upon which the wave-length of "spotted" matched points can be read directly and with high accuracy. The continuous background from the temperature radiation of the carbon rods provides a means of locating exactly, if required, the match point between two very close iron lines. The exact wave-length value of such a match point can be extrapolated directly from linear measurements since the deviation from linearity between any two neighboring lines in the iron spectrum is negligible.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance given them by Miss Dorothy C. Heinzelman in the preparation of the plates for Figs. 1 and 2.

Modifications of Spectrographic Methods for Analysis of Aluminum and Its Alloys

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(Received May 12, 1944)

DURING the past few years several papers[1-6] have been published outlining methods and equipment used for the spectrographic analysis of aluminum and its alloys. It is felt that modifications of these methods which are used in the spectrographic laboratories of the Aluminum Company of Canada, Limited, may be of interest to other workers, especially as many authorities hope that methods of spectrographic analysis will be standardized in the near future. Also of interest may be some of the difficulties experienced in this work; these difficulties will be discussed in an article which will be published later.

At the present time the Aluminum Company of Canada, Limited, has seven spectrographic laboratories in operation, the largest of which has three spectrographic installations and makes an average of over 6000 quantitative determinations per day. At one fabrication plant over 90 percent of the regular alloy analysis is done by spectrographic methods, and it is expected that within the next year nearly 100 percent of all alloy work will be done spectrographically at several of the laboratories. The most recent reduction plants to go into operation have been equipped only with spectrographic laboratories as complete chemical laboratory facilities were not deemed necessary.

STANDARD EQUIPMENT

At present both Hilger medium quartz spectrographs and ARL-Dietert grating spectrographs are being used. The Hilger instruments are used for most analyses on pure aluminum as large dispersion is not needed in this work. The larger dispersion of the Dietert instrument is advantageous for some of the alloy work which is done in the fabrication plants.

Three types of densitometers are being used, the Hilger non-recording microphotometer, the Leeds and Northrup recording microphotometer, and the ARL-Dietert densitometer. Of these three makes of instruments, while all are satisfactory, we have found that the last-mentioned type is most suitable for routine work. The Leeds and Northrup instrument possesses many advantages for development work but because of its critical focusing requirements, this instrument is not used in our routine laboratories.

Spark discharges are used for most analyses on routine samples (except for certain elements present in very low percentages). Both the relatively simple Hilger condensed sparking outfit and the ARL-Dietert heavy duty spark unit are being used. In most cases where careful tests have been made, no appreciable difference in accuracy has been obtained with these two types of source units. For trace elements and powdered samples both the d.c. arc and low voltage a.c. arc are used.

Standard plate and film processing equipment is used throughout and the plates and films are numbered with a numbering box. The latter is operated by allowing small parallel beams of light to pass through perforated numbers and letters, which move in slides.

SPECIAL EQUIPMENT

For all routine analysis on pure metal and alloys the samples are electrodes (diameter $\frac{1}{4}''$ or $\frac{3}{8}''$) which are filed or machined to various shapes. While the usual types of arc and spark stands can be used to mount a few electrodes, such a stand is not satisfactory in a laboratory where a thousand samples of the same type must be analyzed per day. Two types of sparking stands, in both of which the electrodes are mounted horizontally, are used. In both types the electrical leads are attached to the bottom part of the stand which is mounted on the optical

[1] W. R. Koch, Proc. A.S.T.M. **36**, 292–301 (1936).
[2] J. R. Handforth, H. W. Whymper, and W. M. Boulton, Metal Treatment **5**, 3–12 (1939).
[3] A. G. Quarrell, Inst. Met. **67**, 25–47 (1941).
[4] A. R. Striganov, Comptes rendus (Doklady) Acad. Sci. U.R.S.S. **31**, 437–440 (1941).
[5] H. V. Churchill and J. R. Churchill, J. Opt. Soc. Am. **31**, 611–619 (1941).
[6] A. C. Coates and E. H. Amstein, J. Soc. Chem. Ind. Trans. and Comm. **61**, 21–29 (1942).

bench. The top section of the holder is readily removable from, and makes electrical contact with, the lower section by means of sliding members. In each case guards, which may be moved vertically, protect the operator as no discharge can take place until these are lowered.

For the first type, $\frac{1}{4}''$ diameter electrodes are used. They are machined flat with a small chamfer by means of a Shauer Type NAIE high speed lathe. About 300 electrodes may be accurately machined per hour with this type of lathe. The electrodes are fastened in universal clips arranged with suitable ball joints. An aligning device is used in which the electrodes are set up so that they are even with the top of a removable glass gauge and separated by a standard distance equal to its thickness. At the start of each working shift the lower section is adjusted so that the first pair of electrodes is centered on the optic axis, and hence, all succeeding samples will be accurately aligned. Two interchangeable upper sections are used so that while one sample is being exposed the next is set up.

In the type of stand illustrated in Fig. 1 electrodes of $\frac{3}{8}''$ diameter are used. By means of a special milling machine an exact $\frac{3}{4}''$ length section of the electrode is machined down to $\frac{1}{4}''$ diameter, faced, and chamfered. Approximately

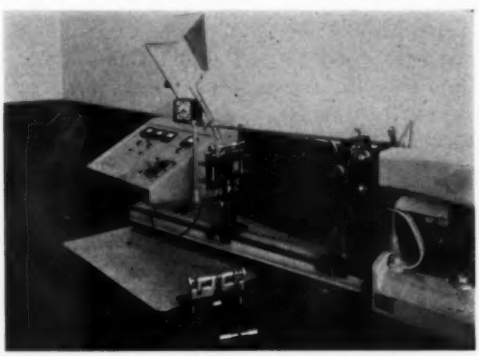

FIG. 1. Typical arrangement of spectrographic accessories illustrating the use of a horizontal spark stand for $\frac{1}{4}''$ electrodes.

200 electrodes may be machined per hour in this machine. When inserted in the electrode stand, the electrode faces are accurately perpendicular, aligned, and separated by 3 mm. More accurate alignment is obtained with this type of stand than with the preceding type. Also water cooling may be more easily provided for the latter type.

At the present time a multiple sparking stand which uses the second type of electrode is being constructed. In this way the interruptions between successive exposures are greatly reduced. By using two spark sources one sample is presparked while the second is exposed. Automatic reset timers control the motion of the electrode holders, the timing of the spark discharges, the movement of the spectrograph shutter, and the movement of the plateholder. With the exception of the setting-up of the electrodes, the operation of the spectrograph is independent of the analyst.

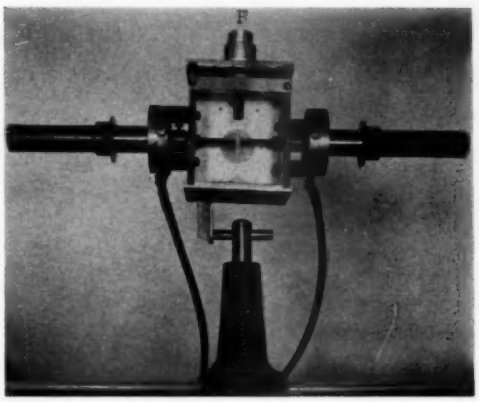

FIG. 2. Ore furnace.

For analyses using arc sources, two types of electrode shapes are used, depending upon the section of the arc stream which is used. Because of the amount of non-conducting oxide formed, it is advisable when using the cathode layer method to machine the electrodes (diameter $\frac{1}{4}''$) to a 60° cone with a flat top of $\frac{1}{8}''$ diameter. The electrodes are pre-arced (electrode separation 6 mm) until a ring of non-conducting oxide is formed. They are then resurfaced by filing so that a clean metal surface is presented to the arc but with the ring of oxide still remaining at the edges. For the most part this prevents wandering of the arc. For certain other applications a 2-mm arc gap is used. In this case flat electrode surfaces are used and very little wandering of the arc is observed. The disad-

vantage of the latter method is the considerable amount of continuous radiation which enters the optical system, necessitating background corrections.

When analyzing certain powders and ore samples, an ore furnace as illustrated in Fig. 2 is used. The powder is placed in the funnel *F*, and a $\frac{1}{16}''$ stream is allowed to flow about $\frac{1}{4}''$ behind the carbon electrodes. A 220-volt alternating current arc is used. This maintains even temperature of the electrodes and prevents fusing of the sample on either electrode. When the arc is struck, a part of the sample enters the arc discharge and is excited. A vertical diaphragm (width = 1.5 mm) placed 4 cm in front of the arc prevents continuous radiation from entering the optical system. When using materials which are not free flowing, the funnel *F* is exchanged for another containing an electromagnetic vibrator to facilitate the flow. The accuracy of the results which are obtained with this method depends on the degree of uniformity of the size and weight of the particles of the sample.

For some internal control analyses where maximum accuracy is not required, the logarithmic spiral method is used. As pointed out by Twyman and Harvey,[7] the difference in the lengths of the lines of the unknown element and the internal standard element is a function of the percentage of the unknown element present in the sample. In order to speed up routine analyses, a direct reading comparator is used to obtain percentages directly. This instrument is essentially a projection machine which throws a magnified image of the spectrum plate onto a horizontal set of scales in front of the analyst. (See Fig. 3.)

A magnification of fifteen times is found to be most satisfactory. The spectrum plate, which is mounted on a mechanical stage, can be moved rapidly in either direction by means of rack and pinion motions. The scale is very similar to a slide rule. The base holds the large slide and smaller slides move in the larger slide. The end of the aluminum internal standard line is determined by moving the large slide until the line is just extinguished by the black area. The points of extinction of the other lines are found in the same way by moving the smaller slides, and the percent concentrations are read from the adjacent scales.

For this type of analysis a slit length of 9 mm is used and by suitably masking the plateholder so that only radiations of certain specified wavelengths reach the emulsion, it is possible to make forty exposures on a $2\frac{1}{2}'' \times 4''$ plate for the analysis of the natural occurring impurities (i.e., Cu, Fe, Si, Ti) in aluminum. This is accomplished by a rack and pinion motion in the plateholder which moves the plate in a horizontal direction so that 4 rows of overlapping spectra are recorded.

By the use of this direct reading comparator and the above type of electrode stands, three analysts can quite easily make 1200 quantitative determinations in an eight-hour period.

When using the usual types of microphotometers and recording either transmission or density values, it is customary to use a graphical calculating board to determine the percentages of the elements that are present. Such calculators have been described by Owens[8,9] and are available commercially. However, for these calculators to be useful for rapid work, it is necessary either that the plate contrast remain constant or that a quick method be devised for plotting the calibration curve. Since our carefully controlled experiments have indicated that most photo-

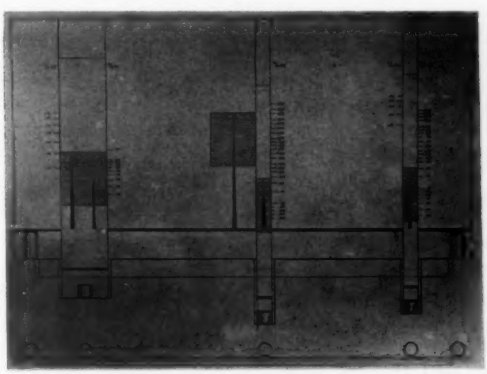

FIG. 3. Arrangement of analytical scales for the direct reading comparator.

[7] F. Twyman and A. Harvey, Trans. Opt. Soc. **33**, 1–8 (1931).

[8] J. S. Owens, Metals and Alloys **9**, 15–19 (1938).

[9] J. S. Owens, Ind. Eng. Chem. Anal. Ed. **10**, 64–67 (1938).

graphic emulsions on plates do not have a constant gamma either from plate to plate or in the varying spectrum regions on one plate, we measure the gamma-value for each plate. Also in high percentage alloy work it is often desirable to use various gamma-values depending upon the percentage range covered by the specification. For these reasons a graphical calculator was built along the lines of similar calculators which are available commercially, but with the following changes.

(1) An accurate mechanical method for plotting the calibration curve.

(2) A suitable arrangement for analyzing many elements in varying concentration ranges and alloys.

(3) Suitable arrangements for completing spectral analyses when it is necessary to use two different gamma-values (one for the internal standard line, the other for the alloying constituent).

The general arrangement of this calculator is shown in Fig. 4.

A sheet of graph paper on which suitable transmission (or density) and log intensity scales have been engraved is placed between two sheets of glass which rest on an angle iron frame. The calibration curve is traced out by a piano wire which is pressed firmly against the lower sheet of glass by small transparent celluloid springs. By means of a parabolic reflector a clear, well-defined shadow of the wire and of the graph paper appears on the upper surface of the glass. The characteristic curve for each plate is plotted by adjusting the wire by means of steel strips which slide freely in grooves machined in the brass bedplate. These steel slides may be firmly clamped in any position. Since the length of the characteristic curve varies, the lower end of the wire is attached to the last slide and the upper end is unattached.

If high gamma-values (i.e., 1.6 to 2.2) are used, the upper end of the brass bedplate should be cut away to form a straight line. Also the lower end of the wire is brought out through the frame, looped back, and fastened to the frame to form a spiral so that an inflection point occurs at zero density. This later change prevents the formation of a small bulge in the toe portion of the curve.

Cross slides, on each of which up to twenty analytical scales may be placed, may be easily attached to the vertical slide. These scales may be fitted into grooves machined in the plastic cross slide so that the equivalence point may be adjusted from time to time. These cross slides may be made exactly parallel with the graph sheet by means of adjustable springs. The alignment is maintained by means of a parallel attachment which is similar to Keuffel and Esser Company's parallel attachment No. 2547.

Continuous use of these calculators in routine analysis during the past three years has shown that:

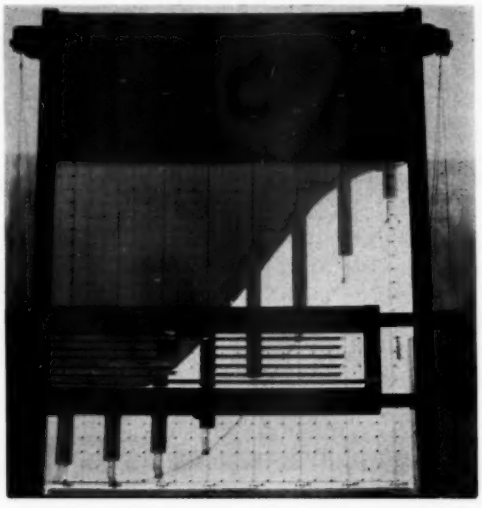

FIG. 4. Modified graphical calculator.

(1) Mechanical plotting is more reproducible than manual plotting, especially when several operators are preparing the calibration curve; in any case, the difference in the results of manual and mechanical plotting is well within the experimental error inherent in the values used in plotting the curves.

(2) Mechanical plotting is much more rapid than manual plotting. The complete process of taking a calibration spectrum, reading the densities of six steps of a suitable line, and plotting the calibration graph requires about ten minutes. Since in most types of analyses approximately 35 samples are placed on each photographic

plate, the extra time per sample allotted to plate calibration is very small.

(3) Since the analyst is working with diffused light instead of reflected light, there is less glare and hence less strain on the operators.

(4) Due to the simplicity of the analytical scale arrangement, we believe that this calculator is as convenient in operation as other calculators which are available commercially.

STANDARD PROCEDURES

The standard methods which are used in the routine laboratories can be illustrated by outlining the methods for pure metal analysis and for a typical alloy.

A. Pure Metal

Samples: Two cylindrical electrodes $\frac{1}{4}''$ in diameter are used. The sparking surface is obtained by carefully machining the ends to a smooth, flat surface with rounded edges.

Spectrograph: Hilger medium quartz spectrograph.

Sparking circuit: A condensed spark is obtained by the following circuit:

(a) Transformer: Hilger F-282, $\frac{1}{4}$ kw, 15,000 volts.
(b) Condenser: Hilger F-283, 0.005 μf.
(c) Self-inductance: Hilger F-285, 0.06 mh.

Spark gap: The electrodes are in an horizontal position and perpendicular to the optical axis. The spark gap is 3 mm.

Distance: Electrode to slit, 45 cm. This distance may be varied slightly depending upon the sensitivity of the photographic plates and the speed of the spectrograph.

Width of slit. 0.035 mm.

Length of slit. 1.9 mm.

Condensing lens. Hilger spherical condensing lens, No. H 439, mounted 2 cm in front of the face of the spectrograph slit.

Photography. (a) 15 seconds, following a prespark period of 15 seconds. With this exposure the Al internal standard line should have a density within the range 0.400 to 0.500. (b) Plate calibration: Copper or nickel d.c. arc, operating at a distance of 50 cm from the slit, is used, the exposure being 15 seconds. If the power supply is taken from an unfiltered rectified source, care must be taken to prevent stroboscopic effects. A modified Jarrell-Ash step sector rotating at variable speeds is used to obtain the step spectrum.

Photographic plates. Spectrum Analysis No. 1.

Plate processing. The plates are developed for $2\frac{3}{4}$ minutes in D-19 at 70°F, fixed for 3 minutes in Kodak acid fixing solution, washed for 3 minutes, swabbed with moist cotton batting, and dried on a plate drier. Dietert processing equipment is used throughout. Spectral lines used. (See Table I.)

B. Alloy Analysis (AC 21S Alloy)

Samples, spectrograph, sparking circuit, spark gap, distance electrode to slit, width of slit, condensing lens, photographic plates, and plate processing are same as in preceding method except that a self-inductance of 0.25 mh is used.

TABLE I.

Spectral lines used		Percentage for equal intensity with standard line	Percentage range covered in analysis
Al	2669.17 I.A.	Internal standard line	
Si	2516.12 I.A.	0.08	0.02 –0.35
	2514.33 I.A.	0.25	0.20 –0.75
Fe	2739.55 I.A.	0.19	0.06 –0.50
	2727.54 I.A.	0.83	0.40 –1.90
Cu	3273.96 I.A.	0.020	0.008–0.15
Ti	3349.41 I.A.	0.030	0.007–0.15
Mn	2593.73 I.A.	0.015	0.006–0.06

Reading of plates: The clear plate setting is adjusted to 100 on an unexposed portion of the plate in the wave-length region of the spectrum line concerned. Transmission readings of the spectrum lines are used to calculate percentage compositions.

Length of slit. 3.8 mm.

Photographing. (a) Exposure: 40 seconds following prespark period of 20 seconds. A modified Jarrell-Ash double-exposure, variable aperture rotating sector is used to give two exposures of different density. The sector opening is set at approximately 45°. With this exposure, Al λ2669 I.A. (full exposure) should have a density within the range 0.425 to 0.525 and Al λ3050 I.A. (interrupted exposure) should have a density within the range 0.525 to 0.625. (b) Plate calibration: Same as for previous method. (c) As greater accuracy is obtained by analyzing duplicate samples (original and duplicate samples once each; *not* the original sample twice) on

TABLE II.

Spectral lines used		Percentage for equal intensity with standard line	Percentage range covered in analysis
Al	2669.17 I.A.	Internal standard line	
	3050.07 I.A.	Internal standard line	
Cu	2824.37 I.A.	2.7	3.25 –4.50
Fe	2613.82 I.A.	0.32	0.30 –1.15
Mg	2776.70 I.A.	0.46	0.20 –0.80
Mn	2672.59 I.A.	0.73	0.50 –1.00
Si	2514.33 I.A.	0.72	0.40 –1.10
Ti	3349.40 I.A.	0.030	0.005–0.08

Reading of plates: The clear plate reading for Mg should be taken at approximately λ2774. Clear plate readings for the other analytical lines may be taken on either side of the spectrum line. The percentages of Cu, Fe, Mn, Mg, and Ti are determined using Al λ2669.17 I.A. as the internal standard line, and the percentage of Si is determined using Al λ3050.07 as the internal standard line. (The densities of the Si and Al λ3050 lines are measured on the interrupted exposure portion of the line.)

Caution: As the density of Fe λ2613 is much higher than that of Al λ2669 care must be exercised in the analysis for iron.

different plates, this is done unless otherwise agreed on by the development laboratory. If original and duplicate samples are analyzed the results are averaged, provided that they are within check limits. (d) One sample of known composition is exposed on each edge of every plate. If the analytical results obtained on this sample differ by more than ½ of the check limit from the known composition of the sample, then the plate is resparked or the analytical results are altered proportionately. Spectral lines used. (See Table II.)

ACCURACY

It may be noted, from the method outlined above for AC 21 S alloy, that rather severe restrictions are placed on alloy analyses, especially when high percentage constituents are present. As experience is gained by the analysts in any particular laboratory, and on a particular alloy, the restrictions are gradually removed for that alloy. While it is not intended that a detailed discussion of accuracy will be given in this paper some comments may be useful.

In Table III an example is given of the results obtained on AC 21 S alloy in a routine laboratory. The average deviations between the individual spectrographic and chemical analyses are

TABLE III.

Sample number	Cu Spec. O*	Cu Spec. D**	Cu Chem.	Fe Spec. O	Fe Spec. D	Fe Chem.	Mg Spec. O	Mg Spec. D	Mg Chem.	Mn Spec. O	Mn Spec. D	Mn Chem.	Si Spec. O	Si Spec. D	Si Chem.
MA 110 A	3.54	3.56	3.72	0.75	0.78	0.77	0.52	0.54	0.56	0.84	0.84	0.80	0.76	0.78	0.72
B	—	3.51	3.78	.74	.77	.78	.50	.51	.55	.83	.83	.83	.77	.78	.72
C	3.66	3.65	3.78	.77	.80	.78	.51	.52	.55	.84	.84	.81	.77	.81	.75
MA 112 A	3.58	3.55	3.65	.80	.79	.80	.55	.56	.55	.84	.81	.84	.79	.77	.76
B	3.55	3.52	3.72	.79	.77	.80	.55	.56	.57	.85	.81	.83	.77	.77	.79
C	3.59	3.66	3.65	.84	.82	.81	.52	.55	.53	.88	.83	.84	.79	.83	.79
MA 113 A	3.66	3.53	3.65	.80	.78	.81	.53	.55	.53	.81	.84	.84	.79	.78	.78
B	3.67	3.60	3.65	.78	.77	.80	.53	.54	.52	.84	.80	.84	.78	.78	.76
C	3.67	3.71	3.72	.80	.83	.80	.54	.55	.52	.84	.85	.82	.81	.82	.76
MA 114 A	3.53	3.62	3.78	.79	.79	.79	.44	.46	.48	.85	.82	.83	.76	.76	.75
B	3.64	3.48	3.72	.76	.76	.78	.50	.49	.51	.82	.84	.83	.78	.72	.75
C	3.59	3.60	3.72	.79	.78	.78	.51	.52	.51	.83	.82	.82	.78	.78	.77
MA 115 A	3.55	3.60	3.59	.77	.77	.74	.50	.54	.52	.84	.85	.82	.77	.78	.74
B	3.67	3.64	3.65	.78	.78	.73	.52	.54	.52	.84	.83	.81	.78	.79	.75
C	3.53	3.52	3.59	.74	.72	.74	.50	.51	.52	.84	.79	.81	.76	.71	.74
Av. dev. of individual spec. result from corresponding chem. result			2.7%			2.4%			3.7%			2.4%			3.8%
Av. dev. of av. spec. result and corresponding chem. result			2.7%			2.2%			3.3%			1.8%			3.4%
Av. total dev. between the 2 spec. values			1.5%			2.0%			3.1%			2.6%			2.4%

* O = Original.
** D = Duplicate.

of the same order as that reported by other workers.[5] In general the results are improved slightly by analyzing in duplicate. It may also be noted that in all cases except that of manganese the "average total deviation" between the two spectrographic values is somewhat lower than the average deviation between the spectrographic and chemical values. As the "average total deviation" is considerably greater than the "average deviation," it may be seen that part of the average deviation between the chemical and spectrographic results is caused by small consistent errors in the routine chemical analyses against which the spectrographic values have been compared or by small shifts in the spectrographic curves.

In analyses where the length of line method is used an average deviation as great as ±15 percent may be obtained. However, if a good analyst is using this method each day and is checked regularly by more accurate methods it is possible to reduce the average deviation to ±8 percent. The greatest difficulty is usually in keeping twelve to fifteen analysts accurately "calibrated" as each one will tend to drift towards either high or low values (the values obtained being quite reproducible for any one analyst).

When using more accurate methods as outlined above, it has been found that a number of errors may affect the results for some alloys. In some cases these errors greatly lower the accuracy of the results unless corrective measures are applied. These errors will be discussed in another article to be published later.

ACKNOWLEDGMENT

The authors are pleased to acknowledge their indebtedness to Mr. R. H. Rimmer, Manager of the General Technical Department, for his active guidance and to Dr. A. Hone who first introduced spectrographic methods in our laboratories and whose ideas have contributed greatly to the success of these methods. They are also indebted to Messrs. W. S. Morrison and L. K. MacIlquaham for help in devising electrical circuits and help in constructing our first graphical calculator, and to Messrs. W. O. Taylor, J. F. Gurney, W. C. Hancock, and others of the various Works Spectrographic Laboratories who have contributed to this work.

Color Tolerance Specification*

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AND

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INTRODUCTION

THE need for a satisfactory method of expressing color tolerance and color fastness becomes increasingly important as means are developed for rapid color measurement. As soon as color can be accurately specified, the next practical requirement is that color tolerances and color fastness be accurately specified, and satisfying one need does not necessarily provide an answer to the other. When color measurement was slow and uncertain, it was sufficient to set up tolerances in sample form. Buyer and seller had to find some basis for agreement, and cases of dispute often depended for settlement on the most persuasive personality involved. But with color specification becoming more commonplace, a specification for color tolerance also becomes necessary. Tolerances for single colors, or for groups of colors, may be set up by studying each color or group separately, but that is a very different problem from the use of a general small-difference formula that can be applied to all colors. Tolerances, whether for purchase or for color fastness, may be expressed as some multiple of an index provided by such a small-difference formula.

One principle must be recognized before any general expression for small color difference can be satisfactorily developed. A general expression must involve judgments of "equality of color difference" and must depend therefore upon color scales that have visually uniform color spacing. Whatever terminology (*6*)[1] is employed must take account of equal color-difference perceptions by reference to some basis providing uniform chromaticity scales. This remains true whether the expression is to cover an over-all color difference, or a difference broken down into terms of its several perceptual attributes.[2]

This report will confine itself to consideration of small color-difference formulas in terms of the attributes of color perception, hue, lightness, and saturation, and those characteristics of light that are their correlates, dominant wave-length, luminous reflectance, and purity. It will leave to future investigators the problem of including other perceptual attributes, particularly those of transparency, glossiness, and luster. Without them a color tolerance specification cannot be considered truly complete, but there is so much to be done before a satisfactory answer can be developed for the more limited problem that we shall not here attempt to do more than acknowledge the limitation.

A number of recent studies relating to colors that are perceptually equal are directly applicable to this work. They include the work of Purdy (*39*) in 1931; of Munsell, Sloan, and Godlove (*30*), (*13*) on neutral value scales in 1933; of Nickerson and Granville (*35*) on the relation of hue sensibility to dominant wave-length change and the relation between saturation and colorimetric purity in 1940; of Wright (*47*) on the sensitivity of the eye to small color differences in 1941; of MacAdam (*27*) on visual sensitivities to color difference in daylight in 1942; of Bellamy and Newhall (*5*) on attributive limens in selected portions of the Munsell color solid in 1942; and of Newhall, Nickerson, and Judd (*32*) in the final report of the O.S.A. subcommittee on the spacing of the Munsell colors in 1943. There have been several studies that concern various transformations of I.C.I. color specifications to produce more nearly uniform chromaticity scales: by Judd (*21*) in the development of a Maxwell triangle yielding chromaticity scales published in 1935; by MacAdam (*25*) regarding projective

* Paper presented at the Winter Meeting of the Optical Society of America, New York, New York, March 2–4, 1944.

[1] Italic numbers in parentheses refer to literature cited at end of this paper.

[2] For a discussion of color concepts refer to "The concept of color," O.S.A. Colorimetry Committee Report, J. Opt. Soc. Am. **33**, 552 (1943), Fig. 3.

transformations of I.C.I. color specifications in 1937 and following; by Breckenridge and Schaub (*7*) on rectangular uniform-chromaticity coordinates in 1937; by Robertson and Milligan (*40*) on a readily visualized system for measuring the color of surfaces in 1941; by Scofield, Judd, and Hunter (*41*) in proposing a method of designating color to the A.S.T.M. paint committee *D*-1 in 1941; by Adams (*1*) on *X*-*Z* planes in the I.C.I. system in 1942; by Moon and Spencer (*29*), (*44*) on a metric based on the composite stimulus in 1943; and by Farnsworth (*12*) as a basis for his color blind studies in 1943. Then there is the work of Helson (*15*)–(*17*) and of Judd (*22*) relating to the effect of illumination on colors, 1938 and 1940; of Nickerson (*37*) on the illuminant in color matching, 1941; and Taylor (*46*) on lighting for the detection of small color differences, 1942.

On the basis of some of the studies mentioned, formulas for expressing small color differences have been worked out. Nickerson (*33*), (*34*) in 1936 based a tolerance formula on Munsell scales of hue, value, and chroma; Judd (*19*), (*20*) in 1939 based one on his uniform chromaticity scale diagram; Scofield (*42*) has modified the Judd formula; and more recently a formula based on Adams' *X*-*Z* plane equations has been developed. In fact a formula for tolerance can be expressed in any system in which the scales are regularly and closely related to perceptually equal steps.[3]

Prior to the present study, Balinkin (*3*), (*4*) contributed more general information than any other single investigator to the study of color tolerance formulas and their relative usefulness compared to judgments of color difference made by a group of observers on a carefully selected series of five pale green tiles. Each tile was carefully measured on several instruments. Then observers were supplied with the five tiles, each numbered in one corner, a form card listing the pairs by number, and were asked, if 1 represented the total difference between two tiles, what number—according to the observers' estimation—would represent the total color difference between each other pair. Sixty observers took part in the test, and Dr. Balinkin felt that the results provided "sufficient proof of the physical aspect of the problem and also a demonstration that a visual conception of color difference may be expressed numerically."

The limitation to five tiles, observed in pairs, was a necessary one at the time the Balinkin studies were made, for even with this limitation the work took months of concentrated effort, with years to clear up many of the details, and prepare the reports. The work developed and presented the use of several formulas, and has been invaluable as a start on tolerance work. However, use of only five colors out of the more than a million colors that a color matcher might distinguish does mean that we should go on and see whether what happened with this very close series of green colors can be repeated with series selected in other parts of the color solid. Ideally the color solid should be statistically sampled, making each selected point the center of a group of spheres increasing in diameter, with colors selected over the surfaces of these spheres to provide a group on which visual judgments and instrumental measurements can be made. Since the present work was started, the possibility of doing that on a modest scale has been discussed. To be thoroughly done such a project would take years of cooperative effort on the part of dye chemists, dyers, psychologists, physicists, and many observers. It is, however, not an impossible job, and may yet be undertaken.

MATERIAL FOR THIS STUDY

As a basis for the present studies there were available samples representative of several series of colors for which color tolerances were desired. All samples were taken from lots that already had been accepted or rejected for color. Before setting up a method as standard, it was decided that the whole subject needed investigation to find out how well the several small-difference formulas could be applied to these samples, how the results of the formulas would compare with each other, and how much dependence could be placed on visual observations. Pending completion of this work, with some basis found for judging which formula should be used, tolerances

[3] The MacAdam report based on the Nutting observations can be made the basis for setting tolerances, but not so directly and conveniently unless an approximate representation of the MacAdam data in 3-dimensional space is employed.

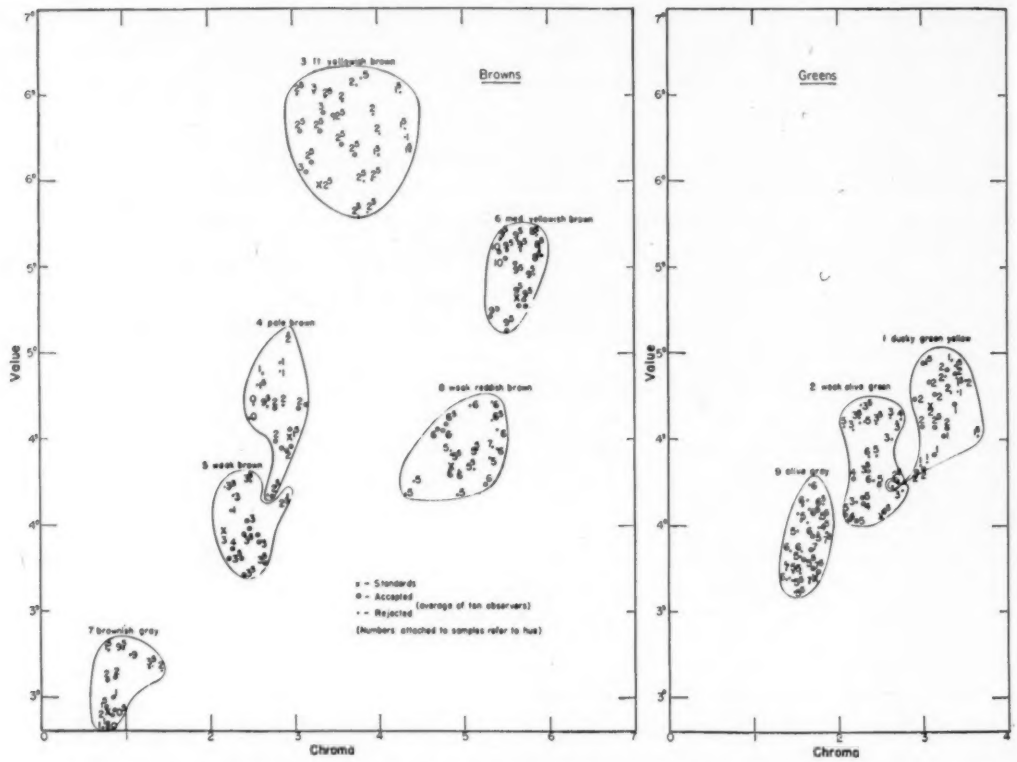

FIG. 1. Scatter diagram of colors in 9 groups of samples plotted for Munsell value and chroma (hue indicated by numbers attached to each sample position). The standard, samples accepted, and samples rejected are indicated.

for specific colors have been set up graphically on I.C.I. color charts in such terms as:

"Y shall not be less than — nor more than —"
"x shall not be less than — nor more than —"
"y shall not be less than — nor more than —"

Such a specification is at best only a stopgap but in many cases it is the first step toward setting tolerance specifications. It is a simplification of a method used many years ago at the National Bureau of Standards, one recommended by MacAdam (*24*) in 1939. And it does not differ too much from the idea suggested by Nutting (*38*) in 1935 of using dominant wave-length and purity for specifying tolerances. For some purposes a method might be employed such as that suggested by Monego (*28*). Or the MacAdam ellipses could have been used (*26*), (*27*). In fact there are several methods that could have been employed as a first step (*8*)–(*10*), (*14*), (*43*), (*45*).

The data with which we had to deal are shown in Table I and Fig. 1. All I.C.I. data were developed from spectrophotometric curves made on the G.E. Recording Spectrophotometer, 400–900 mμ. Samples were paint-covered cloth of near-matt surface, about $2\frac{1}{4}\times3\frac{1}{4}$, with rough edge. Colorimetric calculations were made by the selected ordinate method by use of inked rules on fitted cardboard scales, and checked by weighted ordinates, 380–770 mμ computed by the punch card method reported elsewhere (*23*). The average differences for the two methods on the 187 chromatic samples involved were not more than 1 in the fourth decimal place. Colorimetric data were also computed for Planckian 10,000°K by J. J. Hanlon, then at the Philadelphia Navy Yard. For purposes of this paper we have not yet made full study of the 10,000°K data (which were developed because of discussions regarding the need for using calculations for an illuminant that

TABLE I. Color specifications (I.C.I. and Munsell) for 11 series containing 200 samples included in this test.

Color name	Color series No.	Color order	From spectrophotometric curves: I.C.I. data for C illuminant X	Y	Z	x	y	Munsell renotations H	V	C
Dusky green yellow	1	Std.	0.1532	0.1707	0.1068	0.3556	0.3964	1.8 GY	4.70	3.10
		1	.1442	.1622	.1006	.3543	.3986	2.3 GY	4.58	3.15
		2	.1448	.1620	.1038	.3627	.3945	2.2 GY	4.58	2.99
		3	.1572	.1748	.1167	.3504	.3896	2.0 GY	4.74	2.89
		4	.1745	.1934	.1281	.3518	.3899	1.7 GY	4.95	3.00
		5	.1650	.1840	.1185	.3529	.3936	2.0 GY	4.84	3.09
		6	.1271	.1424	.0893	.3543	.3969	2.1 GY	4.32	2.95
		7	.1268	.1424	.0882	.3547	.3985	2.1 GY	4.32	3.01
		8	.1680	.1882	.1138	.3574	.4005	1.9 GY	4.89	3.40
		9	.1436	.1611	.0965	.3579	.4016	1.8 GY	4.57	3.25
		10	.1701	.1901	.1174	.3562	.3980	1.8 GY	4.91	3.31
		11	.1553	.1738	.1025	.3597	.4028	1.7 GY	4.72	3.38
		12	.1336	.1487	.0882	.3606	.4014	1.2 GY	4.41	3.15
		13	.1409	.1570	.0923	.3611	.4023	1.2 GY	4.52	3.24
		14	.1606	.1778	.1100	.3582	.3964	1.2 GY	4.77	3.15
		15	.1654	.1849	.1103	.3592	.4014	1.6 GY	4.86	3.40
		16	.1632	.1840	.1093	.3574	.4032	2.2 GY	4.85	3.50
		17	.1599	.1788	.1054	.3600	.4027	1.6 GY	4.78	3.42
		18	.1589	.1784	.1085	.3564	.4002	2.0 GY	4.78	3.33
		19	.1666	.1862	.1155	.3558	.3976	1.9 GY	4.87	3.27
		20	.1753	.1943	.1179	.3596	.3985	1.2 GY	4.96	3.35
		21	.1718	.1918	.1159	.3582	.4000	1.7 GY	4.93	3.39
		22	.1386	.1568	.0840	.3654	.4133	1.6 GY	4.51	3.63
		23	.1306	.1442	.0882	.3597	.3973	1.2 GY	4.35	2.96
		24	.1318	.1456	.0874	.3614	.3992	0.8 GY	4.37	3.05
		25	.1220	.1350	.0893	.3522	.3899	1.6 GY	4.22	2.63
		Average	.1518	.1695	.1039	.3561	.3987	1.7 GY	4.66	3.20
Weak olive green	2	Std.	.1086	.1231	.0890	.3386	.3838	4.5 GY	4.05	2.50
		1	.1204	.1368	.1030	.3343	.3798	5.0 GY	4.25	2.50
		2	.1158	.1294	.0973	.3381	.3779	3.9 GY	4.14	2.31
		3	.1163	.1306	.1011	.3342	.3752	4.8 GY	4.16	2.28
		4	.1081	.1218	.0962	.3316	.3734	5.2 GY	4.03	2.21
		5	.1100	.1224	.0970	.3338	.3716	4.3 GY	4.04	2.10
		6	.1275	.1419	.1066	.3391	.3774	3.6 GY	4.32	2.35
		7	.1111	.1240	.1009	.3306	.3690	5.0 GY	4.06	2.08
		8	.1259	.1394	.1092	.3361	.3721	3.8 GY	4.28	2.18
		9	.1323	.1488	.1135	.3353	.3771	4.8 GY	4.41	2.45
		10	.1479	.1646	.1311	.3334	.3711	5.0 GY	4.61	2.30
		11	.1216	.1383	.1093	.3293	.3746	5.8 GY	4.27	2.40
		12	.1303	.1478	.1194	.3277	.3718	6.1 GY	4.40	2.35
		13	.1170	.1292	.0991	.3388	.3742	3.0 GY	4.14	2.20
		14	.1397	.1558	.1123	.3426	.3819	3.2 GY	4.50	2.62
		15	.1201	.1355	.0904	.3471	.3915	3.1 GY	4.23	2.74
		16	.1473	.1647	.1184	.3423	.3827	3.4 GY	4.61	2.64
		17	.1468	.1650	.1194	.3405	.3826	3.9 GY	4.62	2.67
		18	.1482	.1639	.1290	.3360	.3715	3.7 GY	4.60	2.25
		19	.1224	.1369	.0913	.3491	.3905	2.6 GY	4.25	2.69
		20	.1491	.1658	.1191	.3435	.3820	2.9 GY	4.63	2.61
		21	.1470	.1636	.1239	.3384	.3764	3.7 GY	4.60	2.44
		22	.1557	.1716	.1349	.3369	.3712	3.4 GY	4.70	2.26
		23	.1463	.1617	.1339	.3311	.3659	4.8 GY	4.58	2.05
		24	.1503	.1658	.1316	.3356	.3703	3.7 GY	4.63	2.22
		25	.1461	.1603	.1259	.3380	.3708	2.8 GY	4.56	2.17
		Average	.1321	.1474	.1126	.3369	.3761	4.1 GY	4.38	2.36
Light yellowish brown	3	Std.	.2940	.2973	.2035	.3698	.3741	2.5 Y	5.97	3.30
		1	.3090	.3141	.2178	.3675	.3735	2.5 Y	6.12	3.20
		2	.3028	.3081	.2170	.3658	.3722	3.0 Y	6.06	3.14
		3	.3322	.3362	.2332	.3684	.3729	2.5 Y	6.30	3.32

TABLE I.—*Continued.*

Color name	Color series No.	Color order	From spectrophotometric curves: I.C.I. data for *C* illuminant *X*	*Y*	*Z*	*x*	*y*	Munsell renotations *H*	*V*	*C*
Light yellowish brown, cont'd	3	4	.3429	.3490	.2393	.3682	.3748	3.0 Y	6.40	3.38
		5	.3242	.3272	.2160	.3738	.3772	2.3 Y	6.22	3.58
		6	.3312	.3365	.2428	.3638	.3696	2.7 Y	6.30	3.08
		7	.3431	.3473	.2342	.3710	.3757	2.5 Y	6.39	3.50
		8	.3154	.3189	.2032	.3766	.3808	2.6 Y	6.16	3.72
		9	.3556	.3612	.2491	.3682	.3739	2.7 Y	6.49	3.38
		10	.2985	.3010	.1855	.3803	.3835	2.5 Y	6.00	3.83
		11	.3259	.3274	.2190	.3736	.3753	1.9 Y	6.22	3.51
		12	.2994	.3016	.1832	.3818	.3846	2.5 Y	6.01	3.92
		13	.3592	.3638	.2685	.3623	.3669	2.3 Y	6.51	3.03
		14	.3596	.3651	.2595	.3654	.3710	2.8 Y	6.52	3.24
		15	.2780	.2801	.1685	.3826	.3855	2.6 Y	5.82	3.87
		16	.3309	.3325	.2217	.3738	.3757	2.0 Y	6.27	3.58
		17	.3675	.3699	.2435	.3747	.3771	2.1 Y	6.56	3.75
		18	.2751	.2772	.1702	.3808	.3837	2.6 Y	5.79	3.77
		19	.3470	.3479	.2148	.3814	.3824	2.0 Y	6.39	3.95
		20	.3641	.3646	.2425	.3749	.3754	1.6 Y	6.52	4.26
		21	.3334	.3345	.2059	.3816	.3828	2.0 Y	6.28	4.01
		22	.3717	.3745	.2426	.3759	.3787	5.0 Y	6.60	3.80
		23	.3400	.3377	.1996	.3876	.3849	1.4 Y	6.31	4.32
		24	.3213	.3189	.1989	.3830	.3801	1.3 Y	6.16	4.00
		25	.3355	.3317	.1965	.3884	.3840	1.1 Y	6.26	4.32
		26	.3244	.3213	.1871	.3895	.3858	1.3 Y	6.18	4.37
		Average	.3303	.3326	.2177	.3754	.3780	2.4 Y	6.26	3.69
Pale brown	4	Std.	.1574	.1561	.1022	.3786	.3755	1.7 Y	4.50	2.95
		1	.1535	.1522	.1006	.3778	.3747	1.7 Y	4.45	2.86
		2	.1531	.1521	.0989	.3788	.3764	1.9 Y	4.45	2.91
		3	.1557	.1550	.1046	.3749	.3732	2.0 Y	4.49	2.76
		4	.1520	.1512	.0973	.3794	.3776	2.1 Y	4.44	2.93
		5	.1745	.1733	.1107	.3807	.3781	1.9 Y	4.72	3.14
		6	.1312	.1314	.0848	.3777	.3782	2.5 Y	4.17	2.73
		7	.1710	.1706	.1106	.3782	.3772	2.2 Y	4.69	3.05
		8	.1614	.1599	.1024	.3809	.3773	1.7 Y	4.55	2.94
		9	.1699	.1700	.1148	.3737	.3738	2.2 Y	4.68	2.76
		10	.1723	.1716	.1157	.3749	.3733	1.9 Y	4.70	2.88
		11	.1325	.1311	.0868	.3782	.3742	1.5 Y	4.17	2.70
		12	.1895	.1893	.1315	.3715	.3709	1.9 Y	4.90	2.84
		13	.1940	.1924	.1370	.3707	.3675	1.1 Y	4.94	2.83
		14	.1826	.1821	.1329	.3669	.3660	1.6 Y	4.82	2.57
		15	.1878	.1868	.1363	.3676	.3656	1.2 Y	4.88	2.63
		16	.2090	.2090	.1472	.3697	.3698	1.9 Y	5.12	2.87
		17	.1751	.1719	.1286	.3681	.3615	0.1 Y	4.70	2.52
		18	.1749	.1707	.1249	.3717	.3628	9.7 YR	4.69	2.68
		19	.1680	.1652	.1240	.3675	.3612	0.2 Y	4.62	2.43
		Average	.1688	.1677	.1152	.3742	.3715	1.5 Y	4.64	2.79
Weak brown	5	Std.	.1160	.1170	.0838	.3662	.3692	2.8 Y	3.95	2.15
		1	.1010	.1021	.0689	.3712	.3755	3.4 Y	3.71	2.39
		2	.1060	.1073	.0748	.3682	.3723	3.3 Y	3.80	2.22
		3	.1058	.1072	.0721	.3711	.3759	3.4 Y	3.80	2.37
		4	.1154	.1170	.0796	.3700	.3749	3.5 Y	3.95	2.38
		5	.1093	.1112	.0765	.3680	.3745	3.9 Y	3.86	2.28
		6	.1174	.1188	.0789	.3726	.3770	3.3 Y	3.98	2.47
		7	.1202	.1214	.0823	.3711	.3748	3.2 Y	4.02	2.43
		8	.1125	.1132	.0735	.3761	.3784	3.0 Y	3.90	2.58
		9	.1143	.1161	.0753	.3738	.3798	3.7 Y	3.94	2.56
		10	.1053	.1060	.0667	.3787	.3813	3.1 Y	3.78	2.65
		11	.1302	.1313	.0934	.3670	.3700	2.9 Y	4.17	2.28
		12	.1330	.1350	.0975	.3638	.3693	3.5 Y	4.22	2.18

TABLE I.—*Continued.*

Color name	Color series No.	Color order	From spectrophotometric curves: I.C.I. data for *C* illuminant *X*	*Y*	*Z*	*x*	*y*	Munsell renotations *H*	*V*	*C*
Weak brown, cont'd	5	13	.1265	.1252	.0903	.3699	.3660	1.1 Y	4.08	2.25
		14	.1381	.1370	.0953	.3729	.3698	3.4 Y	4.25	2.49
		15	.1322	.1317	.0818	.3823	.3809	2.3 Y	4.17	2.92
		Average	.1177	.1187	.0805	.3718	.3747	3.1 Y	3.98	2.43
		Std.	.2448	.2292	.0977	.4281	.4008	9.5 YR	5.32	5.63
Mod. yellowish brown	6	1	.2396	.2238	.0943	.4296	.4013	9.5 YR	5.28	5.67
		2	.2322	.2182	.0982	.4232	.3978	9.5 YR	5.22	5.31
		3	.2583	.2414	.1018	.4294	.4013	9.4 YR	5.46	5.84
		4	.2415	.2264	.0942	.4297	.4027	9.7 YR	5.31	5.71
		5	.2404	.2243	.0930	.4310	.4022	9.5 YR	5.28	5.74
		6	.2649	.2494	.1103	.4241	.3993	9.6 YR	5.53	5.61
		7	.2233	.2086	.0879	.4297	.4013	9.6 YR	5.12	5.52
		8	.2662	.2526	.1139	.4207	.3992	9.9 YR	5.57	5.51
		9	.2701	.2559	.1188	.4188	.3969	9.8 YR	5.60	5.42
		10	.2726	.2566	.1136	.4240	.3992	9.6 YR	5.60	5.67
		11	.2718	.2567	.1181	.4204	.3970	9.6 YR	5.60	5.52
		12	.2781	.2637	.1241	.4177	.3960	9.7 YR	5.67	5.43
		13	.2782	.2624	.1182	.4223	.3984	9.6 YR	5.66	5.64
		14	.2782	.2573	.1134	.4287	.3966	8.7 YR	5.61	5.90
		15	.2740	.2532	.1103	.4298	.3972	8.7 YR	5.57	5.93
		16	.2875	.2663	.1200	.4267	.3952	8.6 YR	5.69	5.86
		Average	.2611	.2448	.1081	.4254	.3988	9.4 YR	5.49	5.64
		Std.	.0615	.0619	.0609	.3338	.3358	2.2 Y	2.91	0.78
Brownish gray	7	1	.0578	.0580	.0576	.3334	.3348	0.9 Y	2.82	0.72
		2	.0587	.0590	.0578	.3345	.3362	1.2 Y	2.84	0.77
		3	.0629	.0634	.0625	.3333	.3357	1.5 Y	2.95	0.75
		4	.0586	.0586	.0575	.3355	.3352	0.1 Y	2.83	0.78
		5	.0616	.0619	.0620	.3323	.3334	0.5 Y	2.91	0.82
		6	.0665	.0667	.0643	.3366	.3376	1.0 Y	3.03	0.85
		7	.0707	.0714	.0686	.3356	.3387	1.8 Y	3.13	0.86
		8	.0699	.0705	.0680	.3355	.3383	1.9 Y	3.11	0.80
		9	.0624	.0622	.0598	.3382	.3373	0.5 Y	2.92	0.84
		10	.0782	.0787	.0774	.3337	.3360	1.3 Y	3.28	0.80
		11	.0778	.0770	.0721	.3429	.3393	9.2 YR	3.25	1.06
		12	.0795	.0791	.0756	.3395	.3377	9.6 YR	3.29	0.97
		13	.0724	.0735	.0633	.3459	.3515	3.5 Y	3.18	1.28
		14	.0718	.0721	.0598	.3526	.3538	2.1 Y	3.15	1.44
		Average	.0678	.0680	.0647	.3378	.3390	1.1 Y	3.05	0.91
		Std.	.1644	.1448	.0726	.4306	.3792	6.0 YR	4.35	4.85
Weak reddish brown	8	1	.1833	.1636	.0842	.4252	.3795	6.4 YR	4.60	4.81
		2	.1805	.1602	.0859	.4231	.3756	5.8 YR	4.56	4.70
		3	.1794	.1602	.0828	.4247	.3792	6.5 YR	4.56	4.76
		4	.1576	.1365	.0616	.4430	.3836	5.9 YR	4.24	5.26
		5	.1508	.1321	.0622	.4370	.3828	6.2 YR	4.18	4.93
		6	.1707	.1495	.0777	.4289	.3758	5.4 YR	4.42	4.85
		7	.1620	.1420	.0699	.4333	.3797	5.8 YR	4.32	4.93
		8	.1698	.1474	.0680	.4407	.3827	5.7 YR	4.39	5.31
		9	.1637	.1425	.0680	.4376	.3808	5.7 YR	4.33	5.13
		10	.1733	.1508	.0736	.4357	.3792	5.4 YR	4.44	5.17
		11	.1723	.1501	.0799	.4284	.3731	5.0 YR	4.43	4.85
		12	.1863	.1642	.0760	.4368	.3850	6.4 YR	4.61	5.34
		13	.1737	.1522	.0673	.4418	.3870	6.4 YR	4.45	5.40
		14	.1728	.1527	.0668	.4405	.3892	6.9 YR	4.46	5.35
		15	.1963	.1730	.0824	.4346	.3831	6.2 YR	4.72	5.34
		16	.1938	.1715	.0871	.4284	.3791	5.8 YR	4.70	5.08
		17	.1836	.1608	.0739	.4389	.3844	6.1 YR	4.56	5.40

TABLE I.—*Continued.*

Color name	Color series No.	Color order	From spectrophotometric curves: I.C.I. data for *C* illuminant *X*	*Y*	*Z*	*x*	*y*	Munsell renotations *H*	*V*	*C*
Weak reddish brown, cont'd	8	18	.1508	.1319	.0749	.4216	.3689	4.9 YR	4.18	4.30
		19	.1570	.1379	.0766	.4225	.3712	5.2 YR	4.26	4.40
		Average	.1725	.1515	.0747	.4328	.3800	5.9 YR	4.44	5.02
Olive gray	9	Std.	.0983	.1027	.0809	.3485	.3644	7.0 Y	3.70	1.73
		1	.1002	.1045	.0819	.3497	.3646	6.8 Y	3.75	1.71
		2	.0981	.1029	.0794	.3498	.3668	7.5 Y	3.73	1.76
		3	.1060	.1107	.0878	.3482	.3634	7.0 Y	3.86	1.68
		4	.1043	.1079	.0884	.3471	.3589	5.5 Y	3.81	1.57
		5	.1117	.1163	.0925	.3486	.3629	6.5 Y	3.94	1.69
		6	.1066	.1103	.0902	.3472	.3592	5.8 Y	3.85	1.56
		7	.0993	.1025	.0854	.3456	.3570	5.6 Y	3.72	1.54
		8	.1028	.1069	.0913	.3417	.3551	6.8 Y	3.79	1.37
		9	.1069	.1106	.0937	.3437	.3553	5.8 Y	3.85	1.42
		10	.1231	.1285	.1012	.3489	.3642	6.3 Y	4.13	1.81
		11	.0932	.0962	.0796	.3463	.3577	5.6 Y	3.61	1.48
		12	.1119	.1176	.0898	.3504	.3684	7.5 Y	3.96	1.84
		13	.1182	.1215	.0984	.3495	.3594	4.9 Y	4.02	1.63
		14	.1134	.1174	.0910	.3524	.3648	5.3 Y	3.96	1.76
		15	.1141	.1180	.0984	.3452	.3570	5.7 Y	3.97	1.51
		16	.1219	.1267	.1027	.3470	.3607	6.3 Y	4.10	1.65
		17	.1053	.1085	.0892	.3477	.3580	5.0 Y	3.82	1.54
		18	.1253	.1299	.1065	.3463	.3592	6.0 Y	4.15	1.62
		19	.0977	.1006	.0852	.3446	.3548	5.2 Y	3.69	1.40
		20	.1180	.1221	.0951	.3521	.3643	5.6 Y	4.03	1.78
		21	.1232	.1278	.1064	.3448	.3575	5.9 Y	4.12	1.56
		22	.0978	.1010	.0852	.3444	.3556	5.7 Y	3.69	1.42
		23	.0994	.1024	.0862	.3451	.3556	5.1 Y	3.72	1.45
		24	.0972	.1006	.0854	.3432	.3552	6.0 Y	3.69	1.39
		25	.1204	.1243	.1044	.3447	.3561	5.4 Y	4.07	1.52
		26	.1177	.1217	.1011	.3457	.3574	5.4 Y	4.03	1.55
		27	.1313	.1362	.1128	.3453	.3582	5.9 Y	4.24	1.65
		28	.1162	.1192	.0931	.3538	.3628	4.5 Y	3.99	1.76
		Average	.1100	.1140	.0929	.3471	.3596	5.9 Y	3.90	1.59
White	10	Std.	.6623	.6812	.6976	.3245	.3337	3.5 Y	8.49	1.00
		1	.6285	.6440	.6500	.3269	.3350	3.0 Y	8.29	1.14
		2	.6275	.6440	.6313	.3298	.3384	3.5 Y	8.29	1.34
		3	.6059	.6215	.5748	.3362	.3448	3.0 Y	8.17	1.75
		4	.6193	.6361	.6149	.3311	.3401	3.5 Y	8.25	1.44
		Average	.6203	.6364	.6178	.3310	.3396	3.2 Y	8.25	1.42
Black	11	Std.	.0369	.0373	.0423	.3166	.3200	7.0 YR	2.22	0.12
		1	.0333	.0340	.0400	.3100	.3173	*N*	2.10	0.00
		2	.0368	.0379	.0432	.3126	.3211	2.5 GY	2.24	0.11
		3	.0403	.0411	.0471	.3136	.3199	7.5 Y	2.35	0.14
		4	.0446	.0452	.0526	.3133	.3171	2.5 YR	2.47	0.10
		5	.0464	.0466	.0532	.3174	.3188	3.5 YR	2.51	0.20
		6	.0386	.0392	.0422	.3213	.3268	3.0 Y	2.28	0.34
		7	.0450	.0456	.0520	.3155	.3200	9.0 YR	2.48	0.15
		8	.0361	.0367	.0400	.3199	.3254	4.0 Y	2.20	0.29
		9	.0528	.0540	.0568	.3227	.3299	5.0 Y	2.72	0.44
		Average	.0415	.0423	.0475	.3163	.3218		2.37	0.20

TABLE II. Extent of agreement of 10 observers on 11 series of samples classified on a scale of 6, from 1, a "very good match," to 6, a "very poor match." Percentages are shown of samples classed in more than 1 out of 6 groups on this scale.

Color series No.	Number of samples	Percentage of individual samples classed in 1 Group	2 Groups	3 Groups	4 Groups	5 Groups	6 Groups
1	25	—	24	28	36	8	4
2	25	—	—	20	64	16	—
3	26	—	8	31	53	8	—
4	19	—	16	53	16	10	5
5	15	—	13	47	40	—	—
6	16	—	6	56	26	12	—
7	14	—	7	21	65	7	—
8	19	—	—	22	68	5	5
9	28	—	7	4	39	39	11
10	4	—	—	75	25	—	—
11	10	10*	20	40	20	10	—

* One sample used as standard.

might more nearly match observation conditions than I.C.I. *C*). These data, however, are under study in connection with color matching studies involving several illuminants.

The color variation within each set of samples in terms of Munsell hue, value, and chroma was such that on the average about two-thirds of the samples would come within ±0.7 hue step, ±0.20 value step, and ±0.22 chroma step of the average color for each group. A study of Fig. 1 indicates that matches in most groups are made from one direction. Few standards plot near the center of their groups as would be the case if the matches were due to a random scattering. Since over 40 percent of the samples in each group were rejected these figures mean that original tolerances were strict. Yet the tolerances were certainly not so strict as they would have been in the case of expensive woolen or silk materials. Because so few samples were involved in the black and white series they were included only in a few of the studies made.

RESULTS OF VISUAL ESTIMATES

The first thing done, since color differences are made up of three variables, was to correlate the hue, value, and chroma differences against visual acceptance or rejection for each chromatic group in order to see whether the slope of the regression lines for the three color variables would be consistent enough to use as a basis for developing a tolerance formula. Multiple correlations of differences from the standard for hue, value, and chroma were made against acceptance (coded at 2.0) and rejection (coded at 5.0), but although the correlation (P) averaged about 0.62, the slope of the regression lines varied a great deal. However, based on the average results the following Tolerance Index was developed, chroma at 3.0 being the average of all the samples:

$$T_i = C/3\ 0.5\Delta H + 2\Delta V + 2\Delta C. \qquad (1)$$

When the samples were laid out it was impossible to believe that all samples marked "Accepted" and all marked "Rejected" were correct. The logical next step was to have visual estimates remade on the samples that had been measured. The group of matchers that accepted or rejected the original lots agreed, with a number of others, to examine visually the measured samples against the measured standard, and grade them for acceptance or rejection in six groups:

1—Pass, Very good match
2—Pass, Satisfactory match
3—Pass, Borderline
4—Fail, Borderline
5—Fail, Poor
6—Fail, Very poor.

TABLE III. Bias in individual judgments shown by degree to which each individual's scores depart from the average of the first ten observers. Scoring is on scale of 6, from 1, very good, to 6, very poor.

Individual observers	Color series No. 1 Bias	2 Bias	3 Bias	4 Bias	5 Bias	6 Bias	7 Bias	8 Bias	9 Bias	10 Bias	11 Bias	Av. Bias
1	+0.3	+0.7	−0.2	−0.3	+0.3	+0.8	−0.1	+0.2	+0.3	+0.4	−0.7	+0.2
2	+ .4	+ .8	+ .2	− .2	+ .4	+ .4	+ .1	+ .5	+ .3	+ .6	− .1	+ .3
3	+ .1	+ .2	− .2	+ .1	− .1	+ .8	+ .3	− .6	− .4	− .4		0
4	− .5	+ .1	+ .1	+ .2	− .1	− .5	+ .4	− .2	+ .4	+ .6	+ .5	+ .1
5	0	− .6	− .5	− .4	− .3	− .8	−1.3	− .2	− .9	+ .1	− .8	− .5
6	+ .1	+ .4	+ .8	+ .6	0	− .1	+ .8	− .4	− .5	+1.1	− .1	+ .2
7	+ .8	+ .6	+ .8	+ .5	+ .9	+ .9	+ .6	0	+1.0	− .9	+ .4	+ .5
8	− .3	− .9	−1.2	+ .1	− .8	− .1	− .6	+ .6	+ .2	− .7	+ .5	− .3
9	− .7	− .5	+ .5	− .1	− .5	− .6	0	+ .3	0	− .7	+ .1	− .2
10	− .1	− .6	0	− .5	+ .1	− .6	− .2	− .2	− .6	+ .1	− .1	− .2
11	+ .1	− .5	0	+ .1	+ .3	+ .1	+ .4	+ .4	+ .1	+ .6	+ .3	− .2
12	− .1	− .7	− .2	− .1	− .1	+ .2	− .2	+ .1	−1.1	− .4	− .4	− .3

TABLE IV. Correlation results of visual observations by 12 individuals against hue, value, and chroma for 9 series of chromatic colors. Rho square (P^2) is a measure of the multiple correlation.

Observer No.	% P^2 for color series No.									Average
	1	2	3	4	5	6	7	8	9	
1	48	64	66	73	69	73	94	25	48	62
2	42	60	71	79	79	63	94	37	48	64
3	34	72	65	43	48	79	65	33	34	52
4	45	51	69	72	55	84	78	03	49	56
5	60	32	74	80	42	63	85	53	19	56
6	49	21	48	62	29	75	88	28	72	52
7	42	43	60	60	57	83	80	49	41	57
8	31	49	34	75	63	80	82	51	62	58
9	28	34	64	49	51	94	90	53	57	58
10	21	32	77	81	42	66	87	52	34	55
11	47	18	74	41	54	62	63	44	55	51
12	73	23	73	69	41	60	86	55	45	58
Average	43	42	65	65	53	74	83	40	47	57

The standard, about $1\times2\frac{1}{4}''$, was generally held in one hand, or placed in the upper center of the gray background (about 20×24), the samples being picked up one by one, held against or close to the standard, judged, and placed in one of several groups, the groups being reviewed and samples moved again if the observer wished before recording his judgment. He was free, as a color matcher would be usually, to pick up and handle both the sample and standard and turn them to different angles of illumination.

The results vary a great deal, even for those experienced in handling these samples, but substituting the average placement on the 1-to-6 scale in the original correlations against hue, value, and chroma, the average correlation coefficient (P) was raised from 0.62 to 0.81, and the slopes of the regression lines for the contribution made by hue, by value, and by chroma to the total correlation showed much less variation than originally. (No new formula was developed on this basis because by the time this information was available, there was also available information that would indicate that while a new formula might fit these particular data better than others there was no indication that it might fit other data any better than the several formulas already available.)

If we are to measure the performance of any tolerance formula by reference to agreement of its results with those based on visual judgments, we must first know how much variation to expect in visual judgments of small differences. All of the first ten observers were accustomed to making color judgments, several at the National Bureau of Standards, several at the U. S. Department of Agriculture, three of them were accustomed to making the judgments upon which similar samples are regularly accepted and rejected. The first four made their judgments under standard artificial daylight (Macbeth 7500°K) at about 60 footcandles, against a gray background, the others in light from a north window. The same gray background was used for all but two of the observers, who used an oak table top. If space permitted we would tabulate the results, for they are important, but the data given in Table II may be enough to show how little agreement there is between observers as to whether a color difference is small enough to be called a very good match or large enough to be very poor, even when the different observers fail about the same percentage of samples. Several other observers have made these judgments but the average agreement is just as low, so we report here only results for our first ten. There were 11 series of colors, including black and white, and with only two

TABLE V. Correlation (R^2) of 14 observers results against average placement by the first 10 of these observers.

Color series No.	Observer No.														Average
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
1	0.62	0.68	0.73	0.74	0.54	0.54	0.69	0.71	0.71	0.72	0.51	0.16	0.48	0.44	0.59
2	.36	.52	.61	.54	.55	.40	.58	.48	.54	.62	.44	.001	.42	.67	.48
3	.88	.91	.81	.90	.76	.83	.78	.42	.72	.82	.90	.80	.85	.70	.79
4	.86	.97	.65	.86	.79	.87	.62	.74	.66	.78	.78	.77	.87	.79	.79
5	.77	.83	.90	.84	.85	.76	.75	.88	.78	.76	.83	.74	.89	.68	.80
6	.93	.89	.86	.90	.76	.74	.78	.80	.93	.86	.86	.70	.81	.12	.78
7	.84	.88	.74	.82	.81	.88	.75	.93	.90	.92	.76	.95	.93	.77	.85
8	.51	.67	.26	.69	.13	.56	.77	.66	.52	.08	.28	.15	.11	.04	.39
9	.95	.95	.31	.68	.70	.81	.17	.24	.27	.36	.46	.59	.38	.16	.50
Average	0.75	0.81	0.65	0.77	0.65	0.71	0.65	0.65	0.67	0.66	0.65	0.54	0.64	0.48	0.66

exceptions every series contains colors that 10 observers placed in 5 out of 6 possible groups. The disagreement as to placement in a scale of 6 was so great that 75 percent of the samples were placed in either 3 or 4 out of 6 groups. While 10 percent of the samples were put in only two groups, 23 percent of the samples were scattered over 5 out of 6 possible groups; what one observer might call 1, very good, another called 6, very poor. Yet on the average the ten observers accepted or rejected about the same number of samples, showing little consistent bias on the part of individuals toward strictness or leniency. What bias there is is shown in Table III. Bias is defined as the departure of the individual average score from the average of the first ten observers. Table III indicates that no observer is consistently biased on the entire 11 series of colors that were observed.

The average placement of each sample by ten observers provided an index against which hue, value, and chroma differences accounted for an 81 percent correlation ($P=0.81$), but these averages represented such wide variations that it seemed desirable to study correlations of individual scores. If color, as made up of hue, value, and chroma differences, provides the sole basis for judgments of color differences, then correlations of individual placement on a six-step scale against correctly measured hue, value, and chroma differences should give 100 percent correlation and also enable us to tell how each observer weighted the hue, value, and chroma differences in arriving at his judgment of degree of departure from the standard. The multiple correlation method used is that of Ezekiel (*11*); the results for percent P^2 are summarized in Table IV.

The average degree of correlation[4] for the 12 observers varied from a low average for one person of $P^2=0.51$ to a high of 0.64 for another. The average correlations obtained for each color series varied from a low of $P^2=0.40$ for the weak reddish brown series (No. 8), to a high average of $P^2=0.83$ for the brownish gray series (No. 7). If results of calculations from spectrophotometric measurements accurately represent the visual appearance to a smaller tolerance than the differences involved in comparison of these samples, and if color were the only basis these 12 individuals used for judging the differences between samples and standards, then the average P^2 result should be 1.00 instead of 0.57. However, the results are significant, and the b factors we obtained indicate that while judgments show a different weighting of the hue, value, and chroma factors, these differences are much less on the average between individuals than between samples. In other words, the distribution of colors in a single series requires a weighting for the hue, value, and chroma factors that may differ markedly between series. We need more representative statistical samples if we are to develop generalized formulas based on an experimental method.

This material, although not all we might wish it to be, is the best we have to date, and does provide a certain amount of information relating to individual placement of nine chromatic color series that may be studied in relation to estimates obtained by use of several forms of tolerance formulas. Correlations for 14 observers against the average placement of the first ten observers are shown in Table V. They indicate the average correlation for individual observers and for color groups.

RESULTS OF ESTIMATES CALCULATED FROM FORMULAS

Table VI includes small-difference specifications on the material that was observed visually, these specifications being derived by formulas from the data in Table I. Average placement on a scale of 6 according to visual judgments of our first ten observers is included in Table VI for comparison to results by the following tolerance formulas: T_i (Tolerance index) developed as described earlier in this report [formula (1)]; I, developed as an Index of Fading by Nickerson (*33*); I', the Nickerson Index adjusted to agree with Euclidean space, as suggested by Balinkin (*4*); ΔE, the Judd index (*18*); ΔE_S, the Hunter-Scofield index (*42*), a modified form of Judd's ΔE; $\Delta E_{A'}$, a formula based on Adams' "chromatic value" (*1*); and $\Delta E_{A''}$ (chromatic valence), a formula based on Adams' chromatic valence (*2*).

[4] The square of rho (P^2), though lower than P, is used hereafter in this paper for it seems a more useful number than P to use to represent the degree of correlation. P (rho) represents multiple linear correlation, R represents simple linear correlation.

TABLE VI. Small-difference specifications on 9 chromatic and 2 neutral series of colors according to several formulas, each adjusted by a factor so that 1 equals a difference slightly larger than *I* (the Nickerson index of fading, intended to be about ½ of a Munsell chroma step) and slightly smaller than ΔE (the Judd NBS unit, a difference "of some commercial importance").

Color series No.	Color order No.	Index of average visual placement	From tolerance formulas							Index of average formula placement
			Munsell			Judd		Adams		
			(1) f=2.381	(2) f=1.164	(3) f=1.291	(4) f=0.907	(5) f=1.104	(6) f=41.854	(7) f=18.706	
1	1	1.2	1.4	1.8	1.3	1.4	1.4	1.2	1.3	1.4
	2	1.5	1.6	1.8	1.4	1.4	1.6	1.7	1.5	1.6
	3	1.8	1.4	1.3	1.8	2.0	1.4	1.9	1.1	1.6
	4	2.3	1.8	2.2	2.1	2.9	3.0	2.7	2.4	2.4
	5	2.6	1.0	1.3	1.1	1.7	1.8	1.5	1.3	1.4
	6	3.0	2.9	3.6	3.2	3.3	4.2	4.0	3.7	3.6
	7	3.2	2.6	3.4	3.1	3.4	4.2	3.9	3.7	3.5
	8	3.2	2.5	2.5	2.9	2.1	2.8	2.3	2.2	2.5
	9	3.2	1.3	1.4	1.6	1.6	1.4	1.4	1.3	1.4
	10	3.4	2.0	2.2	2.4	2.1	2.8	2.2	2.2	2.3
	11	3.4	1.6	1.3	2.3	1.7	1.5	1.5	1.1	1.6
	12	3.4	2.4	3.1	2.5	3.0	3.1	2.9	2.8	2.8
	13	3.4	2.3	2.7	2.1	2.4	2.1	2.1	1.9	2.2
	14	3.5	1.3	1.6	1.2	1.4	1.4	1.2	0.9	1.3
	15	3.6	2.5	2.5	2.8	2.0	2.6	2.4	2.1	2.4
	16	3.6	3.2	3.1	3.6	2.3	2.7	2.4	2.4	2.8
	17	3.7	2.2	2.0	2.7	1.9	2.0	1.8	1.7	2.0
	18	3.8	1.7	1.7	2.0	1.3	1.5	1.3	1.3	1.5
	19	4.0	1.7	1.9	1.9	1.7	2.3	1.8	1.9	1.9
	20	4.3	3.2	3.6	3.1	2.9	3.7	3.0	2.8	3.2
	21	4.3	2.6	2.8	3.0	2.4	3.3	2.7	2.6	2.8
	22	4.5	3.6	3.5	4.6	4.3	3.0	3.9	2.6	3.6
	23	5.6	3.2	3.8	3.1	3.4	4.0	3.8	3.6	3.6
	24	5.6	3.0	3.9	3.0	3.5	3.7	3.4	3.4	3.4
	25	5.7	4.5	5.1	5.1	4.4	5.9	5.9	5.4	5.2
	Average		2.3	2.6	2.6	2.4	2.7	2.6	2.3	
2	1	1.6	1.5	1.9	1.3	3.3	3.4	1.9	1.9	2.2
	2	1.7	1.9	1.9	1.9	1.8	1.4	1.5	1.3	1.7
	3	2.2	1.8	1.9	2.0	2.3	1.6	1.9	1.5	1.9
	4	3.0	2.1	1.9	2.5	2.6	2.0	2.4	1.9	2.2
	5	3.1	3.6	1.7	3.3	2.9	2.1	2.7	2.2	2.6
	6	3.1	2.8	3.4	2.7	3.2	3.1	2.8	2.6	2.9
	7	3.5	2.7	2.0	3.5	3.6	2.5	3.4	2.6	2.9
	8	3.5	3.1	3.5	3.3	3.6	2.9	3.1	2.8	3.2
	9	3.8	2.2	3.0	2.8	3.6	3.8	3.5	3.4	3.2
	10	3.8	4.1	4.8	4.7	5.6	6.1	5.6	5.2	5.2
	11	3.8	2.8	3.3	2.5	3.7	3.0	2.9	2.4	2.9
	12	4.0	3.9	4.7	3.6	4.9	4.3	4.1	3.6	4.2
	13	4.0	3.2	3.3	3.1	3.0	2.1	1.8	2.1	2.7
	14	4.1	4.0	5.1	4.0	4.5	5.2	6.0	4.5	4.8
	15	4.4	3.5	3.9	3.1	3.2	3.1	3.2	2.6	3.2
	16	4.4	4.5	5.8	4.8	5.3	6.4	5.7	5.6	5.4
	17	4.4	4.2	5.3	4.7	5.1	6.4	5.7	5.6	5.3
	18	4.5	4.5	5.6	4.8	5.9	6.0	5.5	5.2	5.4
	19	4.7	3.9	4.4	3.4	3.9	3.6	3.5	2.8	3.6
	20	4.7	5.0	6.4	5.1	5.7	6.7	5.9	5.8	5.8
	21	4.8	3.7	5.0	4.4	5.4	6.0	5.4	5.2	5.0
	22	4.9	5.2	6.5	5.6	6.8	7.1	6.4	6.2	6.3
	23	5.0	4.9	5.6	5.6	6.5	5.9	6.0	5.2	5.7
	24	5.2	4.7	5.8	5.1	6.3	6.3	5.6	5.6	5.6
	25	5.2	5.4	6.4	5.2	6.0	5.8	5.3	5.0	5.6
	Average		3.6	4.1	3.7	4.4	4.3	4.1	3.7	
3	1	1.2	1.2	1.0	1.2	1.5	2.4	1.7	1.5	1.5
	2	1.4	1.8	1.9	1.7	1.9	1.6	1.2	1.1	1.6
	3	2.0	1.7	2.4	2.6	3.2	3.9	3.3	3.2	2.9
	4	2.5	3.1	4.1	3.5	4.2	5.3	4.4	4.3	4.1
	5	2.6	2.8	3.1	3.0	2.9	3.9	3.3	2.8	3.1
	6	3.1	2.9	3.4	3.2	4.0	4.0	3.3	3.2	3.4

TABLE VI.—*Continued.*

Color series No.	Color order No.	Index of average visual placement	From tolerance formulas: Munsell (1) $f=2.381$	Munsell (2) $f=1.164$	Munsell (3) $f=1.291$	Judd (4) $f=0.907$	Judd (5) $f=1.104$	Adams (6) $f=41.854$	Adams (7) $f=18.706$	Index of average formula placement
3	7	3.5	3.0	3.6	3.6	4.0	5.4	4.5	4.3	4.1
	8	3.5	3.0	3.0	3.8	3.2	3.8	3.8	3.0	3.4
	9	3.6	3.1	4.2	4.1	5.1	6.4	5.2	5.0	4.7
	10	3.7	2.7	2.1	4.4	4.0	3.8	3.7	2.8	3.4
	11	4.0	3.0	3.5	2.8	2.8	3.9	3.2	2.8	3.1
	12	4.0	3.1	2.4	5.1	4.6	4.3	4.4	3.2	3.9
	13	4.1	4.1	5.0	4.8	6.1	6.4	5.3	5.0	5.2
	14	4.2	3.3	4.5	4.3	5.6	6.6	5.3	5.2	5.0
	15	4.3	3.6	3.2	4.8	5.0	3.9	4.1	3.2	4.0
	16	4.5	3.5	3.9	3.4	3.3	4.4	3.6	3.4	3.6
	17	4.6	5.6	6.4	5.9	6.0	8.3	6.7	5.4	6.3
	18	4.9	4.6	3.1	4.1	4.3	3.5	3.5	2.6	3.7
	19	5.3	5.8	6.1	6.4	6.1	7.9	6.7	5.8	6.4
	20	5.3	8.7	9.0	9.2	5.8	7.8	6.2	5.8	7.5
	21	5.3	5.7	5.6	6.4	5.5	6.7	6.8	4.9	5.8
	22	5.4	9.1	10.5	8.0	6.7	9.1	7.4	6.9	8.2
	23	5.6	8.4	8.1	9.2	7.8	8.9	7.4	6.2	8.0
	24	5.7	6.1	6.0	6.5	5.7	6.1	4.9	4.1	5.6
	25	5.8	8.6	8.4	9.3	8.0	8.8	7.1	6.0	8.0
	26	5.8	8.2	7.6	9.4	8.0	8.3	7.2	5.4	7.7
	Average		4.5	4.7	5.0	4.8	5.6	4.7	4.1	
4	1	1.6	0.7	0.7	0.8	0.5	0.7	0.5	0.9	0.7
	2	1.9	0.7	0.8	0.6	0.5	0.6	0.5	0.9	0.7
	3	2.1	1.0	1.1	1.6	1.2	1.0	0.8	0.8	1.1
	4	2.5	0.9	1.0	0.8	0.8	0.8	0.8	0.9	0.9
	5	3.1	2.2	2.5	2.3	2.0	2.8	2.6	2.4	2.4
	6	3.2	3.5	4.1	3.3	3.2	3.8	3.5	3.4	3.5
	7	3.2	2.0	2.4	1.9	1.8	2.2	2.3	2.1	2.1
	8	3.4	0.3	0.4	0.4	0.9	1.0	1.0	1.1	0.6
	9	3.4	1.8	1.9	1.8	2.4	2.0	1.2	0.9	1.7
	10	3.7	1.5	1.9	1.7	2.1	2.1	1.9	1.9	1.9
	11	4.2	3.0	3.4	3.3	3.0	4.0	3.4	3.4	3.4
	12	4.7	2.7	3.4	3.2	4.3	4.4	3.9	3.7	3.7
	13	5.0	3.3	4.3	3.6	4.8	4.8	4.4	4.1	4.2
	14	5.0	3.4	3.7	4.0	4.9	3.9	3.7	3.4	3.9
	15	5.1	3.0	4.4	4.0	5.0	4.3	4.1	3.7	4.1
	16	5.3	3.6	4.9	4.9	6.5	6.9	6.0	5.8	5.5
	17	5.7	4.6	4.8	4.4	4.3	3.1	3.8	3.0	4.0
	18	5.7	4.3	4.8	3.9	3.6	2.8	3.4	2.8	3.7
	19	5.7	4.7	4.4	4.8	4.1	2.9	3.6	2.8	3.9
	Average		2.5	2.9	2.7	2.9	2.8	2.7	2.5	
5	1	1.7	2.9	3.2	2.8	2.6	2.5	2.5	2.2	2.7
	2	1.7	1.5	1.8	1.4	1.5	1.6	1.5	1.5	1.5
	3	1.8	2.3	2.5	2.3	2.1	1.7	2.0	1.5	2.1
	4	1.9	1.8	1.6	2.1	1.4	1.0	0.5	0.9	1.3
	5	2.2	2.0	2.3	1.8	1.4	1.2	1.3	1.1	1.6
	6	2.7	2.1	1.9	2.7	2.1	1.6	1.4	1.5	1.9
	7	3.1	2.0	1.9	2.4	1.7	1.6	1.8	1.3	1.8
	8	3.2	2.5	2.1	3.6	3.1	2.0	2.6	1.5	2.5
	9	3.3	3.0	2.6	3.6	2.6	1.8	2.6	1.7	2.6
	10	3.3	3.5	3.3	4.4	2.4	2.2	3.3	2.2	3.0
	11	3.6	1.8	2.1	2.0	1.9	2.5	2.3	2.2	2.1
	12	4.0	2.0	2.7	2.2	2.5	2.9	2.7	2.6	2.5
	13	5.4	2.6	3.0	2.4	2.5	2.3	2.1	1.9	2.4
	14	5.5	3.7	4.0	3.7	3.7	4.2	3.6	3.9	3.8
	15	5.6	5.3	4.9	6.6	5.4	5.1	5.0	3.6	5.1
	Average		2.6	2.7	2.9	2.5	2.3	2.4	2.0	
6	1	1.5	0.4	0.4	0.4	0.8	0.6	0.4	0.6	0.5
	2	1.7	2.0	1.8	2.8	1.9	2.6	2.2	1.7	2.1

TABLE VI.—*Continued.*

Color series No.	Color order No.	Index of average visual placement	From tolerance formulas							Index of average formula placement
			Munsell			Judd		Adams		
			(1) $f=2.381$	(2) $f=1.164$	(3) $f=1.291$	(4) $f=0.907$	(5) $f=1.104$	(6) $f=41.854$	(7) $f=18.706$	
6	3	1.9	4.0	2.0	2.1	1.2	2.0	1.3	1.7	2.0
	4	1.9	0.9	0.9	0.9	0.6	0.4	0.9	0.4	0.7
	5	2.0	0.7	0.7	1.0	1.1	0.7	0.8	0.6	0.8
	6	2.1	3.3	1.8	1.7	2.4	2.4	2.0	2.1	2.2
	7	2.3	3.6	2.0	1.8	2.1	2.7	2.0	2.1	2.3
	8	3.1	2.6	3.2	2.4	3.6	2.9	2.9	2.8	2.9
	9	3.2	3.0	3.4	2.9	4.2	3.2	3.1	2.8	3.2
	10	3.7	3.8	2.4	2.2	2.9	3.2	2.8	2.8	2.9
	11	3.8	4.0	2.6	2.4	3.7	3.1	2.8	2.6	3.0
	12	3.9	3.0	3.6	3.2	4.9	4.0	3.7	3.4	3.7
	13	3.9	3.9	2.7	2.6	3.7	3.8	3.4	3.4	3.4
	14	5.3	4.6	5.2	4.0	3.1	4.3	3.2	3.2	3.9
	15	5.5	4.5	5.0	4.0	2.9	4.0	2.8	2.6	3.7
	16	5.5	5.0	5.8	4.4	3.8	5.1	4.0	3.7	4.5
	Average		3.1	2.7	2.4	2.7	2.8	2.4	2.3	
7	1	1.6	1.1	1.3	1.0	0.7	0.9	1.0	0.9	1.0
	2	1.7	0.7	0.9	0.7	0.6	0.6	0.8	0.8	0.7
	3	1.9	0.5	0.6	0.5	0.3	0.3	0.6	0.4	0.5
	4	2.1	1.0	1.3	1.1	0.9	0.8	0.8	0.9	1.0
	5	2.2	0.7	0.8	0.8	0.5	0.3	0.3	0.4	0.5
	6	2.3	1.3	1.6	1.2	1.2	1.2	1.5	1.3	1.3
	7	2.6	1.6	2.0	1.8	1.8	2.1	2.4	2.2	2.0
	8	3.1	1.1	1.6	1.6	1.6	1.9	2.1	2.1	1.7
	9	3.3	0.9	1.0	0.9	1.4	0.8	0.8	0.8	0.9
	10	3.8	2.1	3.0	2.9	2.9	2.5	3.6	3.6	3.1
	11	5.3	4.1	4.8	3.9	3.9	3.9	3.8	3.7	4.0
	12	5.3	3.7	4.5	3.6	3.5	4.0	3.9	3.7	3.8
	13	5.8	4.3	4.4	4.7	4.4	3.8	4.7	3.9	4.3
	14	5.9	4.3	4.7	5.8	5.8	4.4	5.1	4.1	4.9
	Average		2.0	2.3	2.2	2.1	2.0	2.2	2.1	
8	1	2.2	2.1	2.8	2.2	3.1	2.8	2.6	2.4	2.6
	2	2.3	2.1	2.4	2.1	3.0	2.2	2.2	2.1	2.3
	3	2.9	2.3	2.9	2.2	3.0	2.3	2.4	2.2	2.5
	4	3.0	2.7	2.4	3.5	4.1	2.4	2.6	1.7	2.8
	5	3.6	1.6	1.9	1.6	2.6	1.9	1.9	1.5	1.9
	6	3.6	1.5	1.8	1.6	1.0	0.9	0.9	0.9	1.2
	7	3.8	0.9	1.0	0.9	1.0	0.6	0.6	0.4	0.8
	8	4.0	3.0	2.6	3.9	3.3	2.8	2.7	2.1	2.9
	9	4.0	2.0	1.8	2.4	2.4	1.6	1.4	1.1	1.8
	10	4.1	3.2	3.2	3.2	2.2	2.3	1.8	1.7	2.5
	11	4.2	2.3	2.8	2.6	1.6	1.4	1.5	1.5	2.0
	12	4.4	4.4	4.5	4.6	2.9	4.3	4.2	3.4	4.0
	13	4.4	4.0	3.6	4.7	3.4	3.5	3.7	2.4	3.6
	14	4.4	4.8	4.8	4.9	3.0	3.2	4.0	2.6	3.9
	15	4.6	4.5	4.8	4.2	3.5	5.4	4.8	4.3	4.5
	16	4.6	3.2	3.7	3.4	3.2	4.3	3.6	3.6	3.6
	17	4.7	3.8	3.6	4.8	3.1	4.3	3.8	3.0	3.8
	18	5.1	5.3	5.3	5.3	3.1	3.7	3.9	3.0	4.2
	19	5.1	4.0	3.8	4.2	2.5	2.7	3.0	2.1	3.2
	Average		3.0	3.1	3.3	2.7	2.8	2.7	2.2	
9	1	1.6	0.5	0.6	0.5	0.5	0.4	0.9	0.6	0.6
	2	2.2	0.6	0.7	0.6	0.5	0.4	1.6	0.6	0.7
	3	2.5	1.0	1.3	1.3	1.1	1.4	2.1	1.5	1.4
	4	3.2	2.2	2.4	2.0	1.5	1.2	2.2	1.3	1.8
	5	3.4	1.7	2.2	1.9	1.9	2.3	2.4	2.2	2.1
	6	3.7	2.3	2.5	2.1	1.6	1.5	1.5	1.5	1.9
	7	3.7	1.9	1.8	1.9	1.7	1.2	1.0	1.3	1.5
	8	3.9	2.3	2.0	3.1	2.5	1.6	1.8	1.5	2.1
	9	3.9	2.9	2.9	2.9	2.4	1.8	1.8	1.9	2.4

TABLE VI.—*Continued.*

Color series No.	Color order No.	Index of average visual placement	From tolerance formulas							Index of average formula placement
			Munsell			Judd		Adams		
			(1) $f=2.381$	(2) $f=1.164$	(3) $f=1.291$	(4) $f=0.907$	(5) $f=1.104$	(6) $f=41.854$	(7) $f=18.706$	
9	10	4.0	2.9	3.9	3.5	3.4	4.3	4.5	4.3	3.8
	11	4.0	2.4	2.5	2.4	1.8	1.7	1.3	1.7	2.0
	12	4.0	2.2	2.6	2.3	2.2	2.8	2.3	2.8	2.5
	13	4.0	3.4	4.2	3.2	3.1	3.4	3.1	3.2	3.4
	14	4.1	2.6	3.3	2.5	2.5	2.9	2.8	2.6	2.7
	15	4.2	3.1	3.6	2.9	2.7	2.6	2.7	2.6	2.9
	16	4.2	2.7	3.6	3.2	3.3	3.9	3.8	3.7	3.5
	17	4.2	2.7	2.5	2.4	1.9	1.5	4.0	1.5	2.4
	18	4.3	3.3	4.3	3.7	3.8	4.4	4.4	4.3	4.0
	19	4.3	2.6	2.4	2.8	2.2	1.6	1.5	1.9	2.1
	20	4.4	2.8	3.7	2.9	3.0	3.6	3.4	3.4	3.3
	21	4.4	3.5	4.3	3.6	3.8	4.1	4.1	3.9	3.9
	22	4.5	2.4	2.0	2.7	2.0	1.5	1.6	1.5	2.0
	23	4.5	2.5	2.4	2.7	2.0	1.4	1.2	1.5	2.0
	24	4.5	2.2	1.9	2.9	2.2	1.6	1.6	1.7	2.0
	25	4.5	3.7	4.4	3.6	3.5	3.6	3.6	3.6	3.7
	26	4.7	3.4	4.1	3.2	3.1	3.2	3.2	3.2	3.3
	27	4.9	3.5	4.9	4.3	4.6	5.4	5.2	5.0	4.7
	28	5.8	3.3	4.2	3.2	3.3	3.5	3.1	3.2	3.4
	Average		2.5	2.9	2.6	2.4	2.5	2.6	2.4	
10	1	2.2	1.9	1.9	1.9	2.4	2.8	2.2	2.1	2.2
	2	2.6	2.6	2.6	3.2	3.5	3.7	2.9	2.8	3.0
	3	3.9	5.3	5.0	6.6	6.9	7.4	6.1	5.6	6.1
	4	4.0	3.2	3.2	4.1	4.3	4.6	3.7	3.6	3.8
	Average		3.2	3.2	4.0	4.3	4.6	3.7	3.5	
11	1	1.3	1.3	1.3	1.4	2.0	1.4	1.5	1.0	1.4
	2	1.9	0.8	1.0	0.9	1.5	0.8	0.9	0.4	0.9
	3	2.0	1.2	1.6	1.2	1.3	1.2	1.3	1.1	1.3
	4	2.3	1.4	1.9	2.0	2.0	2.2	2.5	2.2	2.0
	5	2.8	2.0	2.6	2.4	2.1	2.5	2.9	2.5	2.4
	6	3.9	2.1	2.1	2.2	1.5	1.0	1.2	0.6	1.5
	7	4.2	1.5	2.1	2.0	1.9	2.2	2.5	2.3	2.1
	8	4.7	1.7	1.7	1.8	1.1	0.6	0.9	0.4	1.2
	9	5.2	5.3	5.7	4.8	4.2	4.6	5.2	4.4	4.9
	Average		1.9	2.2	2.1	2.0	1.8	2.1	1.7	

As briefly as possible the concept on which each formula is based is described below, the formula given, and two examples given for computation, using No. 2 and No. 23 of Series 3 to illustrate a small and large difference by the several formulas.

Formulas (1), (2), and (3) are based on the concept that size of color difference may be represented by distance in a 3-dimensional psychological surface-color solid. The scales used in these formulas are equivalent to Munsell hue, value, and chroma; the relations of hue, value, and chroma differ for the three formulas.[5]

The preferred form of the first of these formulas to be published (2) is based upon the assumption that for Illuminant *C* and usual conditions of observing samples similar to those in the *Munsell Book of Color* (*31*), the scales of hue, value, and chroma approximate the relation: 1 value step = 2 chroma steps = 3 hue steps at chroma /5. The formula is given in numbers that make the unit value for the index equal to $\frac{1}{3}$ of a Munsell chroma step. Because this formula does not have the property of a metric in Euclidean space, Balinkin suggested in 1941 that it be modified to give it this property. This

[5] Suggestions regarding differences in relations of value to hue and chroma, depending upon conditions of observation, are discussed in a recent paper (*36*), with illustrations of two such solids, and any final tolerance formula based on this concept should include a term that will provide adjustment in accord with conditions of observation.

modification is expressed in (3), with the result that the relations are approximately as follows: 1 Value step = 1 Chroma step = 3 Hue steps at chroma /5. The size of the unit color difference for the index now becomes $\pi/20$ chroma steps (about $\frac{1}{6}$ chroma step). On Balinkin's series of samples this modified formula agreed better with visual estimations than any of the other equations he used, but from Table VI it may be seen that average results on the nine groups of chromatic color samples used in the present test are the same whether formula (2) or (3) is used. Which will prove to be the better on an adequate statistical sample is yet to be determined.

Based on a statistical analysis of samples in this test (a correlation of hue, value, and chroma against "acceptance" or "rejection") the following relations, expressed in formula (1), were developed: 1 Value step = 1 Chroma step = $\frac{1}{4}$ Hue step at /3 chroma. The unit value for the index equals $\frac{1}{2}$ a chroma step.

These three variations of tolerance formulas are given below, with solutions worked for samples No. 2 and No. 23 of Color Group 3 in Table I.

GIVEN from Table I:

A standard of Munsell notation:

2.5 Y 5.97/3.30

Sample No. 2 of Munsell notation:

3.0 Y 6.06/3.14

Sample No. 23 of Munsell notation:

1.4 Y 6.31/4.32.

The formula for Tolerance Index developed for samples reported in this paper:

$$T_i = C/3(0.5\Delta H) + 2\Delta V + 2\Delta C. \qquad (1)$$

Solution:

$$T_{i2} = 1.05(0.5)(0.5) + 2(.09) + 2(.16) = 0.76,$$

$$T_{i23} = 1.44(0.5)(1.1) + 2(.34) + 2(1.02) = 3.51.$$

The formula for Index of Fading, in preferred form as published in 1936:

$$I = C/5(2\Delta H) + 6\Delta V + 3\Delta C. \qquad (2)$$

Solution:

$$I_2 = 0.63(2)(0.5) + 6(.09) + 3(.16) = 1.65,$$

$$I_{23} = 0.86(2)(1.1) + 6(.34) + 3(1.02) = 6.99.$$

The formula for Index of Fading, in Euclidean form, as suggested by Balinkin in 1941:

$$I' = [(C/5\ 2\Delta H)^2 + (6\Delta V)^2 + (20/\pi\ \Delta C)^2]^{\frac{1}{2}}. \qquad (3)$$

Solution:

$$I'_2 = [[0.63(2)(0.5)]^2 + (6\times.09)^2 + (6.4\times.16)^2]^{\frac{1}{2}} = 1.32,$$

$$I'_{23} = [[0.86(2)(1.1)]^2 + (6\times.34)^2 + (6.4\times1.02)^2]^{\frac{1}{2}} = 7.09.$$

As may be seen from the above examples, it is a very simple matter to obtain a figure for small color difference by the Munsell method if one has the Munsell renotations. And if the Munsell renotations are lacking, they are easy to find from I.C.I. (Y and x, y) data by reference to the charts[6] published by the O.S.A. subcommittee in July, 1943 (*32*).

Formulas (4) and (5) are based on the concept that equality of color differences may be derived from the chromaticity and apparent reflectance of samples when referred to a 3-dimensional figure in which the chromaticity is expressed in terms of Judd's "Maxwell triangle yielding uniform chromaticity scales." In this 3-dimensional figure, Judd assumed distance to be a close measure of the perceptibility of the corresponding color difference. On Fig. 2 the scatter of Munsell samples will give the reader an idea of how the UCS diagram spaces colors.

Because the square root of apparent reflectance is known to correlate well under usual observing conditions with observer's estimates of lightness, the lightness differences are made equal to $k\Delta(Y^{\frac{1}{2}})$ in his formula. For any one dominant wave-length and reflectance, departure ΔS, of the color point from the neutral point on the Maxwell triangle correlates fairly well with the saturation of the color perceived under usual observing conditions. To get the same saturation for dark colors, however, requires a greater departure than for light. Consequently, the variable suggested by Judd for estimates of saturation

[6] The figures are usually read to the nearest 0.5 step of hue and nearest 0.1 step of chroma, with value read to the second decimal place as given in Table II of the O.S.A. report. When adjustments are made for hue and chroma for interpolation between two value charts the results are carried to one decimal place for hue and two places for chroma in order to avoid rejection errors. It is not implied that color differences as small as 0.1 hue step or 0.01 chroma step can be recognized.

differences is $Y^{\frac{1}{2}}\Delta S$, instead of ΔS alone. A term f_g is included to account for the masking of perceived color difference by specularly reflected light. For matt surfaces, f_g is unity, for glossy surfaces it is assumed to equal $Y/(Y+k_g)$, where k_g is a constant referring to the conditions under which the samples are visually observed. Since the samples in this study were near-matt, f_g was assumed equal to 1.

The form of the formula given in (4) is used because of convenience of graphic evaluation.[7] Twice in computing ΔE according to (4) it is necessary to find the square root of the sum of two squares. Hunter suggests that these operations may be done graphically with sufficient precision by use of a pair of dividers and a piece of cross-section paper to get the length of the hypotenuse of the right triangle whose other two sides are known. If one has much work to do, and chooses to use the Judd formula, such short cuts should be followed. If one uses an instrument in which the results may be directly expressed or easily converted to terms approximating the Judd uniform chromaticity scales [as for the Hunter reflectometer—see equations given by Hunter (*18*)], then formulas (4) and (5) may be applied with reasonable directness. If, however, data are in I.C.I. terms, then α and β must be obtained as a preliminary part of either the Judd or Hunter-Scofield formulas. These two formulas are given below and worked out for samples No. 2 and No. 23 of Color Group 3 in Table I.

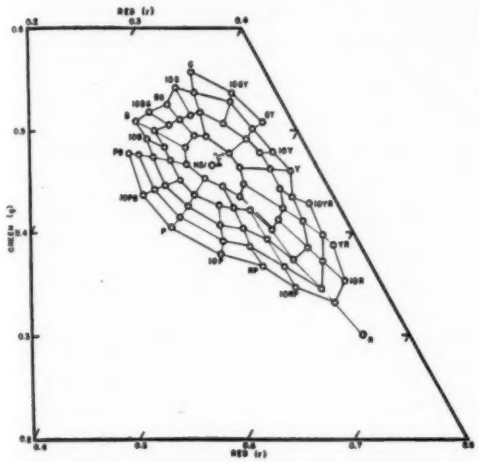

FIG. 2. Munsell 5/ value color samples plotted on Judd's uniform chromaticity scale diagram. In a true uniform chromaticity scale diagram these samples would plot more nearly in concentric circles.

GIVEN from Table I:

For Standard:

$$Y=0.2973;\quad x=0.3698;\quad y=0.3741.$$

For Sample No. 2:

$$Y=0.3081;\quad x=0.3658;\quad y=0.3722.$$

For Sample No. 23:

$$Y=0.3377;\quad x=0.3876;\quad y=0.3849.$$

The Judd formula developed for expressing equality of small color differences, in form convenient for partial graphic evaluation:

$$\Delta E_J=f_g\{[7\,Y^{\frac{1}{2}}[(\Delta\alpha)^2+(\Delta\beta)^2]^{\frac{1}{2}}\cdot 10^2]^2 +[k_1\Delta(Y^{\frac{1}{2}})]^2\}^{\frac{1}{2}},\quad (4)$$

when

$$\alpha=\frac{2.4266x-1.3631y-0.3214}{1.0000x+2.2633y+1.1054},$$

$$\beta=\frac{0.5710x+1.2447y-0.5708}{1.0000x+2.2633y+1.1054},$$

$$f_g=1.0,\quad \text{and}\quad k_1=100.$$

Solution:

$$\alpha_{\text{Std.}}=0.0285;\quad \beta_{\text{Std.}}=0.0457.$$

$$\alpha_{\text{No. 2}}=0.0255;\quad \beta_{\text{No. 2}}=0.0438.$$

$$\alpha_{\text{No. 23}}=0.0400;\quad \beta_{\text{No. 23}}=0.0548.$$

$$\therefore\quad \Delta E_{\text{No. 2}}=f_g\{[7(.3081)^{\frac{1}{2}}(.0030^2 +.0019^2)^{\frac{1}{2}}(100)]^2+[0.98]^2\}^{\frac{1}{2}}=2.10,$$

$$\Delta E_{\text{No. 23}}=f_g\{[7(.3377)^{\frac{1}{2}}(.0115^2 +.0091^2)^{\frac{1}{2}}(100)]^2+[3.58]^2\}^{\frac{1}{2}}=8.60.$$

The Hunter-Scofield modification of the Judd formula was made in order to simplify it, and make it easier to use in practical work. In the paint industry there is considerable use of the Hunter reflectometer, and from results on the

[7] Development of this formula is given in detail by Hunter in (*18*), pp. 519–521.

Hunter instrument α and β may be obtained by the comparatively simple formula:

$$\alpha=\frac{A-G}{A+2G+B}, \quad \text{and} \quad \beta=\frac{0.4(G-B)}{A+2G+B},$$

when A, G, and B designate amber, green, and blue filters of the Hunter instrument.

The Hunter-Scofield formula:

$$\Delta E_{H-S}=[(L_1-L_0)^2+(a_1-a_0)^2+(b_1-b_0)^2]^{\frac{1}{2}}, \quad (5)$$

when $L=100\sqrt{Y}$, $a=7L\alpha$, $b=7L\beta$, and α and β are the same as Judd's.

GIVEN: Data same as for Judd formula (but if measured on the reflectometer instead of spectrophotometer the α and β solutions would be simpler).

Solution: For Standard:

$$L=54.53 \quad a=10.88 \quad b=17.44.$$

For Sample No. 2:

$$L=55.51 \quad a=9.91 \quad b=17.02.$$

For Sample No. 23:

$$L=58.11 \quad a=16.27 \quad b=22.29.$$

$$\therefore \quad \Delta E_{H-S\,\text{No. }2}=[(55.51-54.53)^2+(9.91-10.88)^2+(17.02-17.44)^2]^{\frac{1}{2}}=1.44,$$

$$\Delta E_{H-S\,\text{No. }23}=[(58.11-54.53)^2+(16.27-10.88)^2+(22.29-17.44)^2]^{\frac{1}{2}}=8.09.$$

As may be apparent from the above examples, the Judd formula is not a quick or easy one to use for obtaining an expression of small color difference. The Hunter-Scofield modification, when using the Hunter instrument, is more easily applied, but in comparison to the simplicity of the Munsell formulas, neither is very simple.

Formulas (6) and (7) are based on two types of color space developed by Adams, the first relating to formulas converting I.C.I. tristimulus values X, Y, Z into "chromatic value" space (*1*), the other into "chromatic valence" space (*2*). In each, the illuminant point is the 0 point, therefore values of X, Y, Z must be equalized, instead of being expressed as is usual at present in terms of equal energy at the center of the diagram.

In "chromatic value" space the coordinates are V_Y, (V_X-V_Y), (V_Z-V_Y), V being the Munsell value function recommended by the O.S.A. subcommittee on spacing of the Munsell colors (*32*). The resulting space has the same vertical dimension as Munsell space. The chromaticity of the Adams space is related to Munsell space as shown in Fig. 3. When Adams (V_X-V_Y) is plotted $2\frac{1}{2}$ times the scale for (V_Z-V_Y), radial distance from the illuminant point correlates well with Munsell chroma along any one Munsell hue radius, but equal distances in chroma differ for different hues as is illustrated in Fig. 3.

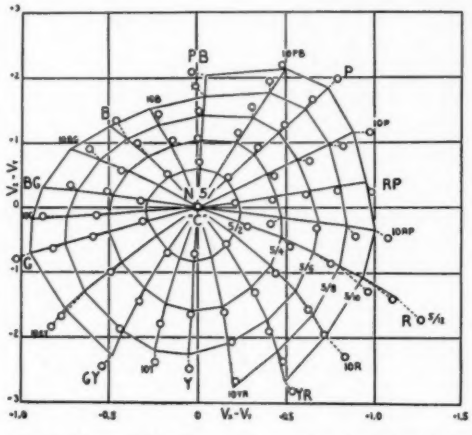

FIG. 3. Munsell 5/ value color samples plotted on Adams' chromatic value diagram. In a true uniform chromaticity scale diagram these samples would plot more nearly in concentric circles.

The Adams' "chromatic value" formula as published by Balinkin (*4*) is:

$$\Delta E_{A'}=[\Delta V_Y{}^2+[7.5\Delta(V_X-V_Y)]^2+[3.0\Delta(V_Z-V_Y)]^2]^{\frac{1}{2}}$$

but the form in which we have used it is:

$$\Delta E_{A'}=[(k\Delta V)^2+[\Delta(V_X-V_Y)]^2+[0.4\Delta(V_Z-V_Y)]^2]^{\frac{1}{2}}. \quad (6)$$

Since (V_X-V_Y) in Adams space equals an average of 8.75 Munsell chroma steps, and in order to approximate the Value-Chroma relationship of (2), where $\Delta V=2\Delta C$, k was fixed at $2/8.75=0.23$.

Below are worked out samples No. 2 and No. 23 of Color Group 3 in Table I.

GIVEN: From Table I:

For Standard:

$X=0.2940$; $Y=0.2973$; $Z=0.2035$.

For Sample No. 2:

$X=0.3028$; $Y=0.3081$; $Z=0.2170$.

For Sample No. 23:

$X=0.3400$; $Y=0.3377$; $Z=0.1996$.

Solution: Read value from tables of Munsell value *vs.* I.C.I. Y for C illuminant[8] after X and Z have been adjusted to $X=Y=Z$ for C illuminant (instead of $X=0.98041$, $Y=1.00000$, $Z=1.18103$). Or read X and Z directly from value tables adjusted to include the correction that will allow these values to be plotted with the illuminant at the center of the diagram.

For Standard:

$V_X=5.99$; $V_Y=5.97$; $V_Z=4.71$.

For Sample No. 2:

$V_X=6.07$; $V_Y=6.06$; $V_Z=4.84$.

For Sample No. 23:

$V_X=6.38$; $V_Y=6.31$; $V_Z=4.67$.

Then obtain (V_X-V_Y) and (V_Z-V_Y) as follows:

For Standard:

$(V_X-V_Y)=+0.02$; $(V_Z-V_Y)=-1.26$.

For Sample No. 2:

$(V_X-V_Y)=+0.01$; $(V_Z-V_Y)=-1.22$.

For Sample No. 23:

$(V_X-V_Y)=+0.07$; $(V_Z-V_Y)=-1.64$.

$$\therefore\quad \Delta E_{A_{\text{No. 2}}}=[[0.23(.09)]^2+(.01)^2+[0.4(.04)]^2]^{\frac{1}{2}}=0.028,$$

$$\Delta E_{A_{\text{No. 23}}}=[[0.23(.34)]^2+(.05)^2+[0.4(.38)]^2]^{\frac{1}{2}}=0.178.$$

Adams' "chromatic valence" space (*2*) was developed to make radial distances, when plotted with a scale factor of $2\frac{1}{2}$, more nearly equal to changes in Munsell chroma than they are in "chromatic value" space. If it is "assumed that the sensitivity of three sets of retinal receptors is determined by the respective tristimulus values, and the sensitivity of all three depends on the same mean between general and local values of Y" then "chromatic valence" space is defined by V_Y, $[(X_c/Y)-1]V$, and $[(Z_c/Y)-1]V$. The formula used for expressing tolerance in Adams' "chromatic valence" space is:

$$\Delta E_{A''}=[(k\Delta V)^2+(\Delta W_X)^2+(0.4\Delta W_Z)^2]^{\frac{1}{2}}, \quad (7)$$

when

$$W_X=[(X_c/Y)-1]V; \text{ and } W_Z=[(Z_c/Y)-1]V.$$

Since the average W_X unit equals about 4 chroma steps, in order to adjust the equation to the relation $V=2C$ as in (2), the constant k becomes $2/4=0.5$. (The data were also calculated at $k=1$, but this weights the value by too much, for it gave an average correlation when compared to visual results of only 0.37 for R^2 against the higher correlation of 0.52 when k is equal to 0.5.)

GIVEN: Same as for (6):

Solution: Adjust X_c and Z_c (by eliminating C illuminant factors 0.98041 and 1.18103), and obtain value for Y factor from Table II of Newhall report (*32*).

For Standard:

$X_c=0.2998$; $Y=0.2973$; $Z_c=0.1723$; $V=5.97$.

For Sample No. 2:

$X_c=0.3089$; $Y=0.3081$; $Z_c=0.1837$; $V=6.06$.

For Sample No. 23:

$X_c=0.3468$; $Y=0.3377$; $Z_c=0.1690$; $V=6.31$,

and obtain W_X and W_Z.

For Standard:

$W_X=+0.05$; $W_Z=-2.51$.

For Sample No. 2:

$W_X=+0.02$; $W_Z=-2.45$.

For Sample No. 23:

$W_X=+0.17$; $W_Z=-3.15$.

[8] See Table II of reference (*32*).

Then substitute in formula:

$$E_{A''\text{No. 2}}=[(0.5\times.09)^2+(.03)^2+(0.4\times.06)^2]^{\frac{1}{2}}=0.06$$

$$E_{A''\text{No. 23}}=[(0.5\times.34)^2+(.12)^2+(0.4\times.64)^2]^{\frac{1}{2}}=0.33.$$

It may not be clear from the above examples how comparatively simple the method is for obtaining an expression of small color difference by either (6) or (7). Actually the use of either (6) or (7) is much more simple than using the Judd method, and results for (6) can be obtained easily and directly from I.C.I. (X, Y, Z) data with the use of Table II in the Newhall report (*32*) and two tables similar to this one which are adjusted for $X=1.0$ and $Z=1.0$. For neither (6) nor (7) is it necessary to obtain (x, y) ratios. As for a comparison of the Adams (6) and Judd (4) methods for relative accuracy relating to chroma, one can see by reference to Figs. 2 and 3 that the Judd UCS diagram shows about a 2-1 ratio for chroma on the red and blue-green axis, while the Adams diagram for chromatic value shows about a 2-1 ratio in chroma for the yellow and purple-blue axis. The Adams "chromatic valence" formula (7) is concerned more nearly with equal chromas, but is more work than (6).

In order that results of these seven formulas may be compared, the foregoing results are adjusted as shown in Table VII so as to produce a unit value that is approximately the same for each formula.

TABLE VII. Tolerance indices adjusted so that they may be compared with each other.

From formula No.	Factor f	Sample No. 2 Tolerance index from formula	Sample No. 2 Formula $\times f$	Sample No. 23 Tolerance index from formula	Sample No. 23 Formula $\times f$
(1)	2.381	0.76	1.81	3.51	8.36
(2)	1.164	1.65	1.92	6.99	8.14
(3)	1.291	1.32	1.70	7.09	9.15
(4)	0.907	2.10	1.90	8.60	7.80
(5)	1.104	1.44	1.59	8.09	8.93
(6)	41.854	0.028	1.17	0.178	7.45
(7)	18.706	0.06	1.12	0.33	6.17

TABLE VIII. Correlation (R^2) of tolerance indices by 7 formulas (1) to (7) against average visual placement of samples by 10 observers.

Color series No.	By formula: Munsell (1) R^2	Munsell (2) R^2	Munsell (3) R^2	Judd (4) R^2	Judd (5) R^2	Adams (6) R^2	Adams (7) R^2	Average R^2
1	0.52	0.49	0.42	0.43	0.40	0.37	0.39	0.43
2	.45	.42	.53	.55	.52	.53	.62	.52
3	.71	.58	.51	.67	.53	.65	.55	.60
4	.76	.78	.79	.77	.51	.71	.57	.70
5	.40	.48	.33	.40	.58	.50	.57	.47
6	.58	.86	.75	.48	.87	.75	.64	.70
7	.91	.90	.90	.92	.87	.86	.84	.89
8	.45	.35	.448	.0009	.20	.21	.14	.26
max.			.51 .44		.004 .28			
min.			.22 .26		.008 .06			
9	.73	.53	.71	.58	.32	.21	.36	.49
Average	0.63	0.60	0.60	0.53	0.53	0.54	0.52	0.56

COMPARISON OF VISUAL AND MEASURED TOLERANCES

Having obtained a small-difference index for each sample by each of seven formulas, and knowing about how much work is involved in using each formula, we would now like to know which formula agrees best with average visual judgments. Results of correlation against the average visual placement made by ten observers are shown in Table VIII.[4] As may be seen, the degree of correlation varies much more in relation to the color group than it does in relation to the formula used. As might have been expected, since it was based on the original acceptance or rejection of the samples under consideration, the T_i formula gives the best average results, $R^2=0.63$. The I and I' formulas, based on additions of hue, value, and chroma differences, come next at $R^2=0.60$. The Judd formula, and Scofield's variation of it, give an average of $R^2=0.53$, Adams' "chromatic value" at $R^2=0.54$, and Adams' "chromatic valence" at $R^2=0.52$.

About the Judd formula, it should be noted that if it were not for color group 8, results by the Judd formula would average 0.60 as they do in the Munsell type formula, but in color group 8 the formula seems to break down. Since it was realized early in this work that the slightest difference in instrument measurements, especially on the Standard, might change the results considerably, computations for the No. 8 series were made again for formulas (2)–(5) for the maximum and minimum of three readings used for the Standard sample. But although this causes considerable difference in the degree of correlation, it does not seem to be the cause for the breakdown in the application of formula (4).[9]

[9] Dr. Judd comments on this breakdown in the Inter-Society Color Council's Discussion Session on Small Color Differences, published in the Am. Dyestuff Rept. **33**, 231 ff. (1944).

Results of correlation for tolerance formulas given in Table VIII may be compared with results of correlations for individual observers given in Table V.

DISCUSSION AND CONCLUSIONS

Because color differences involved in setting tolerances are small it is necessary that color measurements be very accurately made. It is desirable to measure standard and samples at the same time if this is at all possible in order to avoid difficulties due to individual and instrumental variation. Certainly the measurement used for the standard should be on a representative spot, otherwise wide variations may seem to occur (as the authors are convinced they occur in the present data) that are not due to observations or to the small-difference formulas used, but rather to variation in sample and measurement.

Statistical methods of multiple correlation, perhaps curvilinear, applied to a statistically adequate group of color samples should provide a formula for expressing color differences in which the constants may be based upon experiment. One problem seems to be to locate an "adequate sample," and another to isolate the pertinent variables.

For the samples studied, there were found wide variations among individuals in classifying the relative sizes of small color differences, but for some series in the present study certain individuals seem to be able to place the differences in order that agrees very well with the average results for the first ten observers (see Table V). These results when correlated against hue, value, and chroma differences average fairly high for most individuals, for according to the data P^2 varied only between 0.51 and 0.64 for individuals, but between 0.40 and 0.83 for the several color series (Table IV). Thus a particular series of samples may seem to give results that prove the formulas not adequate, when the fault may lie with the sample distribution or the accuracy of their measurement rather than with the formula.

Average results obtained by correlation of seven small-difference formulas against visual observations vary between $R^2=0.52$ and 0.63 for the formulas, not far from the figures for individual observations correlated against hue, value, and chroma. The average differences for the color series vary a great deal for the tolerance formulas, just as they did by individual observation, with one group of colors averaging an index of $R^2=0.26$ while another color group averages $R^2=0.89$.

For the nine chromatic series studied the Munsell formulas give results that correlate closer to average observations by a few percent over results for the other formulas. Formula (2) is the quickest and easiest of the Munsell formulas to apply, and therefore is preferred although results for formula (1) apply best to the nine color series studied. The Judd, Hunter-Scofield, and Adams formulas give results that average about the same, although the Judd formula would equal the Munsell if it were not for a breakdown in series No. 8. The Munsell formula (2) is easy and quick to apply, the Adams formula (6) is also easy and quick to apply. The Judd formula (4) takes the longest. It will depend upon the form of one's color data which formula should be selected to give the most efficient results in time and accuracy.

If comparative results are to be made from one laboratory to another, the use of any one of the formulas would undoubtedly give more consistent results than observations made by different individuals, but it should not be expected that results by formula will always agree with an individual observer's judgment. Results by use of a formula can be repeated between laboratories to the degree that measurements of identical samples can be made and calculated to give identical results.

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